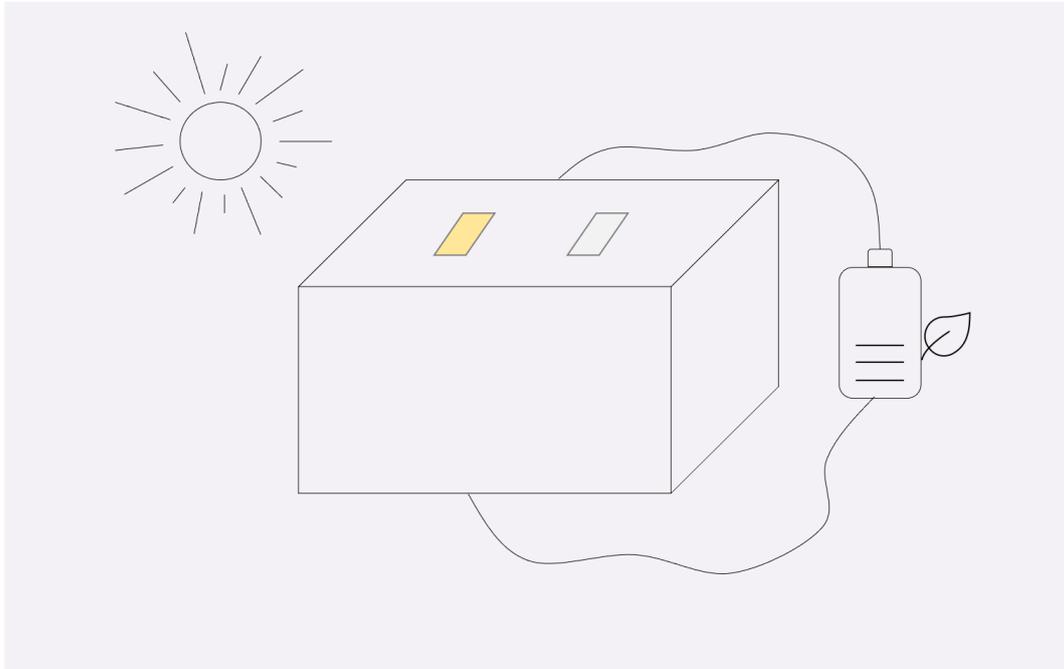
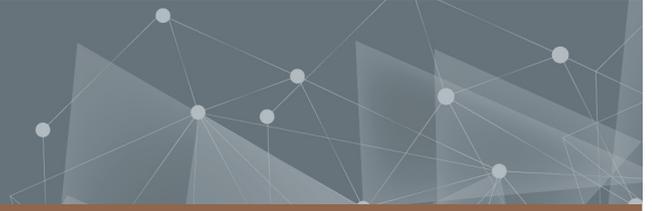




CHALMERS
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Characterisation of Molecular Solar Thermal (MOST) Energy Storage Materials in Miniature Windows

Master's thesis in Materials Chemistry

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CHALMERS UNIVERSITY OF TECHNOLOGY
INSTITUTE OF MATERIALS SCIENCE BARCELONA
Gothenburg, Sweden 2022
www.chalmers.se

MASTER'S THESIS 2022

**Characterisation of Molecular Solar Thermal
(MOST) Energy Storage Materials in Miniature
Windows**

CLARA SZOLNOKY



CHALMERS
UNIVERSITY OF TECHNOLOGY

Department of Chemistry and Chemical Engineering
Division of Applied Chemistry
Kasper Moth-Poulsen Research Group
CHALMERS UNIVERSITY OF TECHNOLOGY
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Characterisation of Molecular Solar Thermal (MOST) Energy Storage Materials in
Miniature Windows
CLARA SZOLNOKY

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Master's Thesis 2022
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Cover: Visualisation of the model house designed and constructed for use in the
outdoor setup of this Master Thesis project.

Typeset in L^AT_EX
Printed by Chalmers Reproservice
Gothenburg, Sweden 2022

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Abstract

Finding and developing alternative ways of capturing and storing energy which lead us in the direction of a more sustainable society is one of today's major challenges. One of these emerging methods is by using molecule solar thermal energy storage (MOST) systems. The principle of the system is a photo-switching process which occurs when the parent molecule is irradiated causing it to form a high energy isomer. As the isomer switches back to the original molecule, energy is released in the form of heat. These molecules can be integrated into different types of matrices such as solutions and films. In this Master's thesis, the MOST-system are investigated by incorporating the MOST-molecules or photo-switches in thin polystyrene films and monitoring the absorbance of the photochromic materials as a function of film thickness when subjected to irradiation.

The project is divided in to two parts; the first consisting of small scale tests of the films in lab. Specifically two molecules are investigated, a norbornadiene and an azobenzene. The photochromic materials are exposed to both LED light using a solar simulator and natural solar radiation for various amounts of time over a number of days and the absorbance is monitored to understand the behaviour of the molecules in films. The second part of the project consists of integrating the materials as windows on a larger scale in a model house and observing the effects of the indoor environment of the house by measuring temperature.

The discoveries from the first part of the project show that the absorbance of the films generally decrease over time with increasing film thickness. When exposed to natural solar radiation, the norbornadiene molecule showed a significant level of degradation compared to the azobenzene. The azobenzene was therefore selected for further testing in the windows of the model house. The experiments from the outdoor setup demonstrated that it is highly likely that the windows containing the MOST-molecules have an affect on the heating of the indoor environment during the night. However, the differences were still small and requires further investigation with larger concentrations of the molecule.

Keywords: Solar energy storage, Photochromic materials, Photoswitches, Norbornadiene, Azobenzene

Acknowledgements

I would like to extend my gratitude to my supervisor and examiner Kasper Moth-Poulsen who presented the opportunity for me to carry out my Master Thesis in Barcelona, Spain back in October 2021 after having worked in his research group during the Summer and Autumn alongside my studies. Professor Moth-Poulsen has been a great support in my move to Spain and all throughout my thesis work. He has also given interesting insight in the research and upcoming MOST-projects that I will continue to work on during the Summer of 2022 in Barcelona.

I would also like to thank the Institute of Materials Science of Barcelona (ICMAB-CSIC) for allowing me to conduct my thesis in their premises and to Professor Mariano Campoy-Quiles' group of which the PhD-students and Post Doctorates have provided valuable guidance throughout my project.

Lastly, I would like to say a special thank you to Eulàlia Pujades who welcomed me to ICMAB and has offered great support through administration and organising of the materials for the project.

Clara Szolnoky, Gothenburg, June 2022

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

| | |
|--------|--|
| ANK | Azobenzene |
| CAD | Computer-aided Design |
| DHA | Dihydroazulene |
| MOST | Molecular Solar Thermal Energy Storage |
| NBD | Norbornadiene |
| PMMA | Polymethyl methacrylate |
| QC | Quadricyclane |
| UV/Vis | Ultraviolet/Visibile |

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1

Introduction

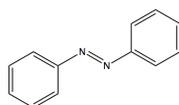
Molecules that are able to photoswitch have shown great potential in storing and releasing energy from irradiated light. The energy from absorbed photons is stored chemically in the bonds of the so called Molecular Solar Thermal Energy Storage molecules (MOST-molecules) in their isomeric state, and can be released as heat upon switching back to the parent configuration. The molecular structure will furthermore dictate how stable the isomer is at room temperature and therefore different photo-switching molecules are able to store energy for longer och shorter periods of time [2].

One major benefit of MOST-molecules is that they can easily be incorporated into solvents and solids since they do not phase change. Instead, their chemical state changes by charging and discharging in cycles, which means they are able to efficiently store energy for specific periods of time. By incorporating MOST-molecules in a transparent polymer matrix such as polystyrene, a composite is formed which has the ability to absorb solar radiation and release it as heat. Future applications of such MOST-materials could for example be in windows which have the ability to sustainably improve energy systems in buildings [2].

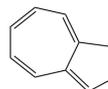
The Kasper Moth-Poulsen Research Group at Chalmers University of Technology carries out a significant part of their research within this area, with multiple projects taking place simultaneously. These projects include the synthesis of the various MOST-molecules, which are mainly norbornadienes (NBDs), and additionally testing of the MOST-systems. Collaborating research groups have also synthesised other photo-switching molecules such as azobenzenes (ANKs) and dihydroazulenes (DHAs), which have been sent to the research group at Chalmers. General structures of these MOST-molecules are shown in Figure 1.1. For this specific project, these three types of MOST-molecules will be integrated into a polymer matrix respectively, more specifically polystyrene, for the purpose of testing the materials in both a solar simulator and a "real world environment". The outline of the project is presented more specifically in the sections below.



(a) Chemical structure of unsubstituted Norbornadiene.



(b) Chemical structure of unsubstituted Azobenzene.



(c) Chemical structure of unsubstituted Dihydroazulene.

Figure 1.1: General chemical structures of the three MOST-molecules studied in this project.

1.1 Aim

The aim of this master thesis project can be divided into two sub-objectives, each with several question formulations which are specified in *Specification of Issue Under Investigation*. The first sub-objective is to test the MOST-molecules (NBDs, ANKs, and DHAs) in polystyrene (PS) coatings on small scale poly(methyl methacrylate) (PMMA) substrates. This will be used to analyse the photo-switches as a function of film thickness and molecule concentration of the coatings in order to compare the different MOST-molecules.

Based on the discoveries of the first sub-objective, the second sub-objective is to incorporate the MOST-molecules into a polystyrene matrix on larger PMMA panels. These MOST-materials will then be integrated as windows in a model house exposed to natural solar radiation in order to observe the effects of the "indoor climate" of the box.

1.2 Specification of Issue Under Investigation

For the two sub-objectives, there are a number of questions to be answered. Regarding the first sub-objective, which is testing the MOST-materials on a small scale, the following questions are formulated,

- How does film thickness and molecule concentration of the coatings impact on the photo-switches of the MOST-molecules?
- How do the photo-switches of the various MOST-molecules incorporated in polymer matrices compare to each other?

For the second sub-objective, which is testing the MOST-materials on a larger scale in a model house, the questions are as following,

- How does absorption/half-life of the MOST-molecules affect the indoor climate of a model house?
- What is the temperature difference between the indoor climates of the model house created by the MOST-windows compared to plain, non-functionalised windows?

- What is the difference in colour of the MOST-materials over time?

1.3 Limitations

One important aspect that will however not be dealt with in this project is the heat flux through the MOST-materials. The heat flux will have a contribution to the properties of the indoor climate in the model house and would therefore be valuable to measure. The reason this is not included in the project is because it has proven to be difficult to create a baseline for which reliable heat flux measurements can be performed. Additionally, edge effects of the windows contribute to varying heat flux results which are often inaccurate compared to the rest of the material. To avoid this, one would need to increase the sizes of the panels substantially to ensure that the measurements become more uniform. This was determined to be out of scope for the project.

2

Theory

When it comes to global energy consumption, the development of energy storage solutions is of critical need. In modern societies, buildings are the largest consumers and a great deal of this consumption is constituted by heating and cooling. This demonstrates the importance of creating on-demand energy absorption and release, which paves the way for the development and use of molecular solar thermal energy (MOST) systems that are able to store energy for short (hours) and long term (years) use [1].

The principle of the system works by converting a molecule from a lower energy state to a higher using radiation, storing the absorbed energy chemically in the bonds of the metastable molecule. This is called a photoswitch and the application of such systems has been mainly studied on the norbornadiene-quadricyclane (NBD-QC) switch. However, more recently other photoswitching molecules have been proposed such as azobenzenes and dihydroazulenes. In this thesis project, these three photoswitches have incorporated and studied in polystyrene thin films and a theoretical background is presented below [1].

2.1 Photoswitching Molecules and Photochromic Materials

Norbornadiene-quadricyclane (NBD) is a negative molecular photo-switch which absorbs sunlight at wavelengths close to 450 nm. Upon radiation a switch from the NBD to the metastable quadricyclane (QC) is induced. Over time, the molecule returns to the lower energy state upon which energy is released as heat. The absorbance of the NBD decreases upon irradiation which is why it is a so called negative photo-switch. The parent molecule (NBD) and isomer (QC) are shown below in Figure 2.1 [2].

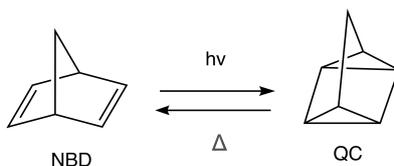


Figure 2.1: Norbornadiene (NBD) - quadricyclane (QC) system.

The unsubstituted NBD shown in Figure 2.1 has been discovered to not be useful for MOST-applications since the absorbance band does not overlap with the solar spectrum. This can be altered by adding donor-acceptor groups which makes the absorbance of the NBD red shifted. More specifically, an aromatic substituent has shown to give a more beneficial solar spectrum overlap. The two NBDs studied in this project are abbreviated NBD4b and NBD4c and the chemical structure is shown in Figure 2.2 [2].



(a) Chemical structure of NBD4b.

(b) Chemical structure of NBD4c.

Figure 2.2: Chemical structures of the two NBD-photo-switches studied in this project.

The difference between the two NBDs shown in Figure 2.2 is the substituent on the phenyl ring. This gives the compounds varying properties such as half-life ($t_{1/2}$) and absorbance maximum (λ_{max}). The molecule NBD4b absorbs at a wavelength of 374 nm, whilst NBD4c absorbs at 454 nm. And the half-lives differ significantly; 6.6 hours for NBD4b and 0.64 hours for NBD4c. This is summarised below in Table 2.1. Both molecules have since previously been studied in MOST-applications as they have a good solar spectrum overlap. For solid states films it is beneficial to have a half-life between 4 - 8 hours, making NBD4b a suitable candidate for window applications [11].

Azobenzenes (also known as azothiophenes) are another type of photoswitching molecule which have shown great potential for photochromic materials and MOST applications. The backbone of the molecule consists of two phenyl rings conjoined by a double bond between two nitrogen atoms. Their potential in MOST applications is mainly due to the azobenzene unit being chemically stable against UV/Vis radiation and at moderate temperatures. When the molecule is radiated by a specific wavelength, the photoisomerisation of the azobenzene is induced and it switches from a trans to a cis conformation. The use of this property can be beneficial for various photoresponsive effects. Additionally, by adding electron withdrawing and donating groups to the molecule, it creates a highly asymmetric electron distribution in the conjugated system giving the molecule useful optical properties. The three different azobenzenes studied in this project are abbreviated ANK240, ANK241 and ANK242 and are shown in Figure 2.3 [3].

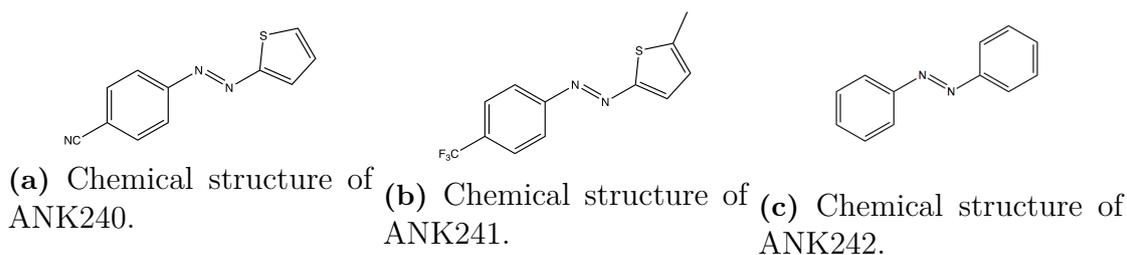


Figure 2.3: Chemical structures of the three ANK-photo-switches studied in this project.

The difference between them structurally are the substituents of the azothiophene backbone, as shown in Figure 2.3. ANK240 and ANK241 have both a phenyl and cyclopentene group with a sulfur, whilst ANK242 has two phenyl groups attached to the double bonded nitrogens. ANK240 consists of a cyanide group attached to the phenyl ring, whilst ANK241 instead has a trifluoromethyl group on the phenyl group and additionally a methyl group attached to the cyclopentene. These structural differences result in varying properties of the MOST-molecules such as absorbance maximum, i.e. the wavelength at which the molecule absorbs irradiated light, as well as the half-life. These have been summarised, together with NBD4b and NBD4c, below in Table 2.1 [4].

Table 2.1: Absorbance maximum (λ_{max}) and half-life ($t_{1/2}$) of MOST-molecules in solution.

| Property | NBD4b | NBD4c | ANK240 | ANK241 | ANK242 |
|----------------------|-------|-------|--------|--------|--------|
| λ_{max} [nm] | 374 | 454 | 379 | 382 | 364 |
| $t_{1/2}$ (25°C) [h] | 6.6 | 0.64 | 3.28 | 4.04 | 3.52 |

What is interpreted from Table 2.1 is that the three azobenzene derivatives have similar absorbance spectra as well as half-lives. However, between the two norbornadiene compounds, the properties differ relatively largely. Note that the specified half-lives are based on the molecules in solution at 25°C. Despite this, these values give a good indication on the behaviour of the molecules in MOST-applications.

As the MOST-molecules are integrated in a polystyrene matrix, the photochromic materials have the ability to absorb and release energy from incoming radiation. The materials are fabricated by applying a thin coating of the viscous solution onto a substrate which can further be used in window applications. The technique used for this is described below.

2.2 Polymer Processing Techniques

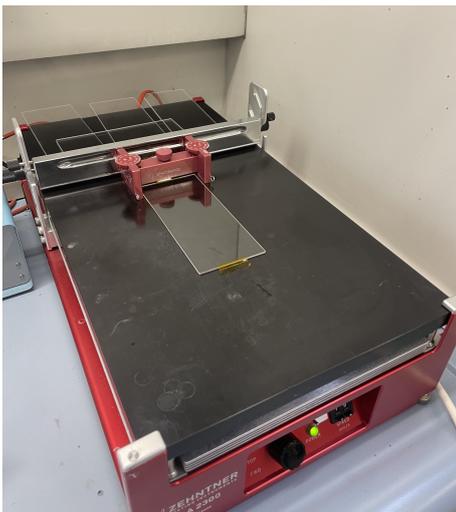
There exists various ways of processing polymers or plastics. Factors that dictate the technique chosen include quantity and production rate, dimensional accuracy and

surface finish, form and amount of detail, type of material and the size of the product. When processing plastics there are generally three different phases; heating, shaping and cooling. The polymer must first be softened or melted, then formed under some form of constraint and finally cooled to hold its shape. It is important to differ between thermoplastics and thermosetting materials as the first can be remelted and reformed, whilst the latter does not change shape upon reheating due to a chemical reaction during shaping [5].

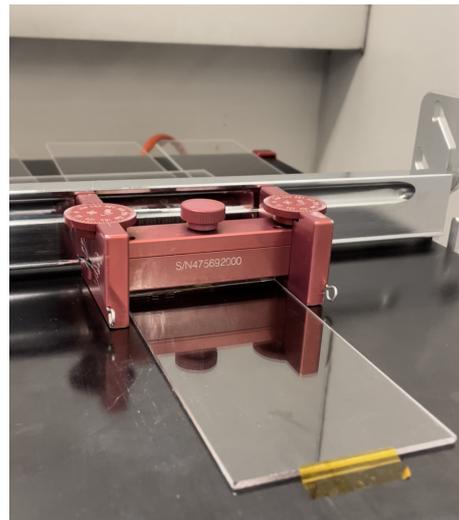
Polymer processing techniques include, but are not limited to thermoforming, extrusion-based processes, injection and blow molding. Coating processes are also important techniques which involve applying a polymeric material onto a substrate and coating the surface of the substrate. More specifically, the technique dealt with in this study is blade coating of the photochromic materials onto a poly(methyl methacrylate) substrate [5].

2.2.1 Blade Coating

In order to achieve a thin, homogeneous polymer coating on a flat substrate, blade coating is an appropriate technique that can be applied. The setup (pictured in Figure 2.4) includes a stationary blade, which can be set at controlled heights, and a hot plate which can be altered to different temperatures to achieve certain coating results. The actual thickness of the coating is determined by a combination of design geometry and operation conditions. These parameters include concentration of the polymer solution, which in this case is polystyrene, volume of polystyrene solution applied to the substrate, speed of the blade and temperature of the hot plate. In this project, the coating thickness as a function of speed was chosen to study, keeping the other mentioned conditions constant [6].



(a) Image of blade coater with hotplate visible.



(b) Image of large PMMA substrate and blade.

Figure 2.4: Images of blade coating instrument used in the project.

In Figure 2.4 the blade coating instrument is shown together with the blade that was used to coat the substrates. Pictured is the larger PMMA panels used for the windows of the model house. The blade is placed on top of the hotplate and the substrate is secured at the base of the blade using thermal tape. The temperature of the hotplate can be regulated and the coating speed can be set between 1 and 60 mm s^{-1} . The viscose liquid is pipetted on to the substrate at the very base of the blade which is then pushed forward by a moving part at the selected speed. Depending on the velocity, different coating results are achieved.

2.3 UV/Vis Spectroscopy

Ultraviolet/Visible (UV/Vis) spectroscopy is an analytical method based on the absorption of electromagnetic radiation in the ultraviolet and visible spectral range with wavelengths between 200 - 800 nm. The instrument used is a spectrometer which contains a light source in which irradiated light passes a monochromator. The monochromator consists of lattices and a prism which scatters and filters the incoming light respectively from the light source. The monochromator then transmits light at a specific wavelength that passes a vial containing the sample. A photomultiplier or detector measures the intensity of the monochromatic light that passes the sample. A schematic representation of a UV/Vis spectrometer can be seen in Figure 2.5. The analysis is usually repeated several times with light of different wavelengths which is later monitored on a computer [7].

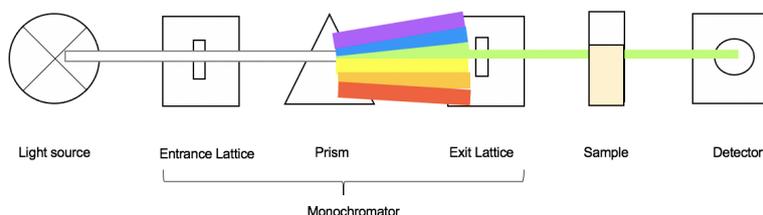


Figure 2.5: Schematic representation of a UV/Vis spectrometer.

The result obtained consists of a UV/Vis spectrum with absorbance on the y-axis and wavelength on the x-axis. The spectrum shows the absorbance of light when the sample is irradiated at different wavelengths and therefore is able to provide information on the concentration of a substance in the sample. In this project the photochromic materials are irradiated with light of wavelengths between 200 - 700 nm [7].

The relationship between the concentration of a substance and its absorbance can be described by Lambert-Beers' law and is given by the following equation

$$A = \epsilon \cdot l \cdot C \quad (2.1)$$

where A stands for the absorbance of the substance, l for the length of the cuvette, ϵ for a molar absorption or extinction coefficient (which is characteristic for the absorbent substance and absorbed wavelength) and C for the concentration of the sample. Equation 2.1 assumes the form $y = kx$ and thus a linear regression can be used to determine how the sample follows Lambert-Beer's law at a certain wavelength. By knowing the length of the cuvette, the concentration and by measuring the sample, the molar extinction coefficient (ϵ) can be determined for each compound. The extinction coefficient can then be used to determine the concentration

of MOST-molecule needed to achieve a certain absorbance. The desired absorbance of the films is dependent on the application [7].

Transmittance and absorbance are two common measurements used in spectroscopy. They can be related to each with the following equation

$$A = 2 - \log(\%T) \quad (2.2)$$

According to Equation 2.2, at absorbance $A = 1$ there is 10% transmittance and at $A = 2$ there is a 1% transmittance. This means that at these absorbances, 10% and 1% of light passes through the sample respectively. Due to the logarithmic behaviour of the equation, absorbances above $A = 2$ will have low impact on the difference in transmittance. For this reason an absorbance of $A = 2$ is selected as the base of the calculations for the MOST-molecule concentrations and weight percentages [8].

2.4 Solar Energy and Device Design

Solar energy is a renewable, freely available energy source and provides a sustainable option in the ongoing energy crisis. The abundance of solar energy is far greater than any other renewable energy source and the sun emits it at a rate of 3.8×10^{23} kW, out of which approximately 1.8×10^{14} kW is intercepted by the earth. For reference, the average annual consumption of a household is 8000 - 10000 kWh which means that you could power 18 billion households yearly just on solar power [9, 10].

The design and selection of materials for the model house were done in cooperation with Professor Angela Sasic Kalagasidis, who is a Building Physics professor and leads a research group within Building Physics Modelling at Chalmers University of Technology. The design is based on a real world application and the materials used were to replicate a modern day house to a certain extent. The goal was to construct an energy efficient and simple setup, however with a reliable baseline for measurements.

The programs used for the computer-aided design (CAD) of the model were AutoCAD and Microsoft Powerpoint. The design includes two open "cavities" or boxes in which the windows (sample and reference window) are placed at the openings. It is on the inside and outside of these boxes where the temperature and UV/Vis measurements take place. Between the open spaces as well as on each side of the openings are thick styrofoam insulations (30 cm). A 2 cm layer of plaster is placed over the styrofoam on each side and finally a reflective material covers the entire box excluding the windows to minimise heating of the boxes through convection of the walls. Drawings of the model (not to scale) are shown below in Figures 2.6, 2.7 and 2.9 with dimensions indicated.

2. Theory

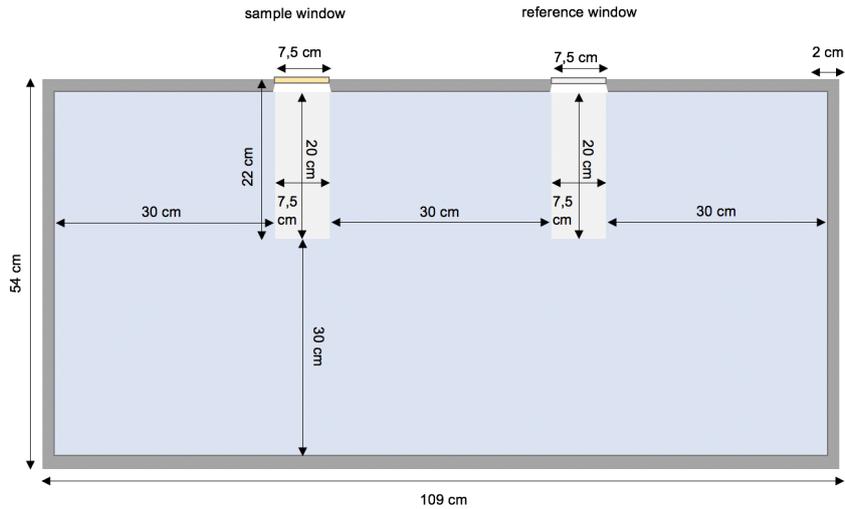


Figure 2.6: Side view of model house with measurements indicated (not scaled).

First, the side view of the model house is visible in Figure 2.6. The blue coloured area indicates the styrofoam insulation, the dark grey frame is the plaster material and the two light grey rectangular areas are the "cavities" for measurements. At the openings of the boxes, the windows are placed. For the purpose of monitoring changes of the indoor environment, both a sample and reference window are used to detect differences.

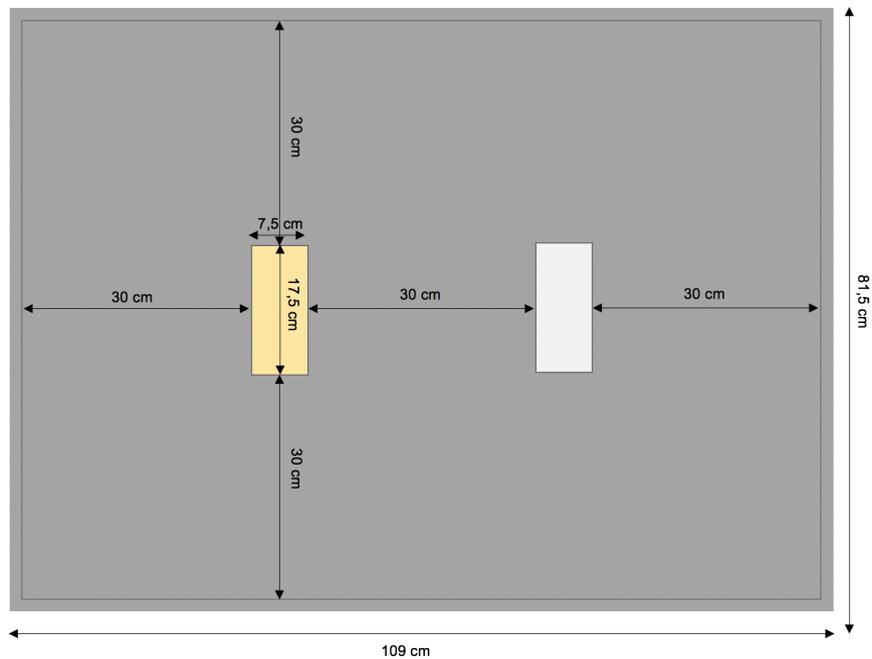


Figure 2.7: Top view of model house with measurements indicated.

Second, Figure 2.7 shows the top view of the model with the windows more clearly visible. The dark grey area is the roof consisting of plaster. The reason for placing

the windows on the roof of the model is to ensure minimal shading effects as well as achieving a more even incidence of sunlight over the day.

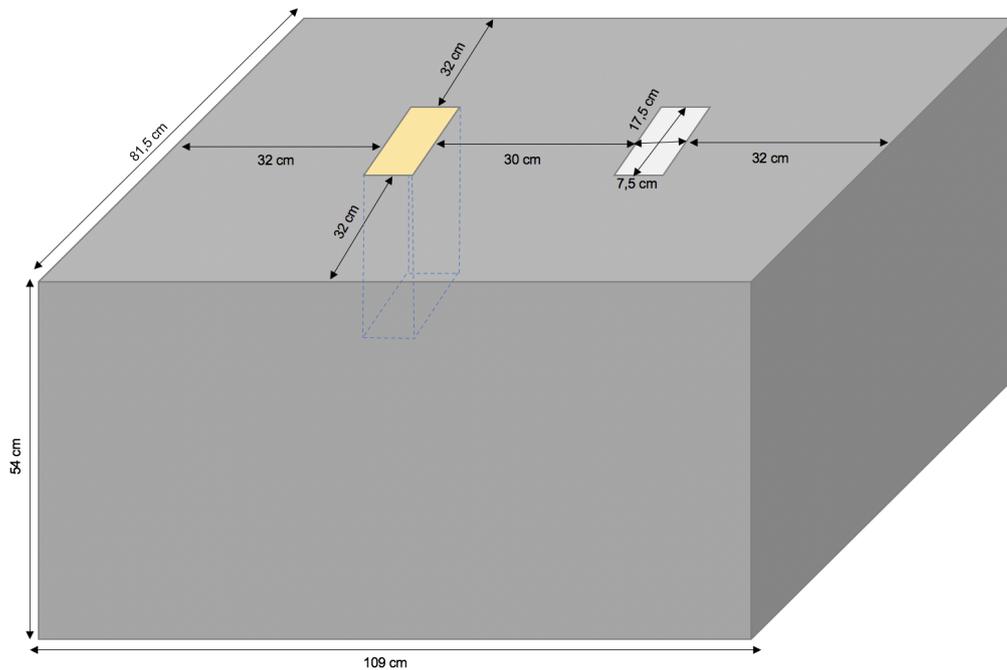


Figure 2.8: 3D view of model house with measurements indicated.

Third, a three dimensional model of the house is shown in Figure 2.8 with dimensions indicated. Here once can also see what the cavity looks like inside the box (shown with a blue dotted line). Although the drawings are not 100% to scale, it still gives a feeling of the sizes of each part and how they compare to each other. In relation to the size of the model, the windows and cavities are quite small.

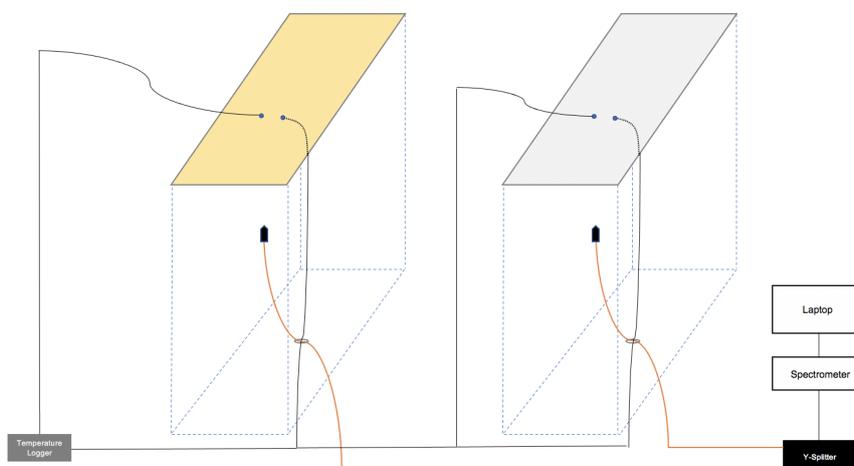


Figure 2.9: Overview of cavities in model house with instruments indicated.

2. Theory

Lastly, the cavities of the model are shown more clearly in Figure 2.9. The two instruments used for measurements are a UV/Vis spectrometer together with fiber optic cables which are pointed perpendicular toward the windows, as well as a temperature logger with thermocouples. The thermocouples are attached on the outside of each window as well as on the inside of each cavity.

3

Methods

The first part of the project was based on "small scale testing" of the MOST-molecule photo-switches, NBD4c, NBD4b, ANK240, ANK241, ANK242 and DHA, incorporated into polystyrene (PS) matrices on poly methyl methacrylate (PMMA) substrates with dimensions of 75 x 25 x 2 mm. The PS/photoswitch films were applied to the substrates using a blade coating instrument, and by varying the speed of the blade different coating results were achieved. Thereafter, the molecular photo-switches were induced using LED lights and monitored with a UV/Vis spectrometer. By comparing the photo-switches of the various types of MOST-molecules as a function of film thickness and molecule concentration, it was possible to assess which of the compounds would be interesting to study on a larger scale.

The second part of the project was based on larger scale testing of the MOST-materials incorporated in a model house. The design and materials of the box were based on heat transfer models to create a reliable baseline for measurements. The outdoor set up consisted of a heavily insulated box with two cavities acting as rooms of the house with a reference and sample window directly exposed to solar radiation over a defined period of time. By measuring the indoor and outdoor temperatures of each room and comparing them to each other the solar heat gain from the MOST-materials could be determined. Additionally, fibre optic cables attached to a UV/Vis spectrometer monitored the photo-switches and the colour change of the materials over time.

3.1 Materials

The MOST-molecules used in this project were previously synthesised by various research groups as listed below:

- i. Norbornadiene/Quadricyclane [NBD/QC] (NBD4c, NBD4b) (synthesised at Chalmers University of Technology, Kasper Moth-Poulsen group [11])
- ii. Azothiophenes (ANK240, ANK241, ANK242) (synthesised at University Giessen, Wegner group [12])
- iii. Dihydroazulene/Vinylheptafulvene [DHA/VHF] (synthesised at University of Copenhagen, Nielsen group [13])

Solvents used were purchased from VWR and polystyrene (MW 192 000 g mol⁻¹) was bought from Sigma-Aldrich. The PMMA substrates (of both the smaller and larger dimensions) were ordered from Mucho Plastico (a local plastic supplier in

Barcelona, Spain).

The blade coater was of the model Zehntner ZAA 2300 with an 8 cm wide blade (Model number: S/N475692000). A Mitutoyo Digimatic micrometer (0.0001 mm) was used to measure the film thicknesses of the coatings. Initially, a Wavelabs SINUS-70 solar simulator containing LED lights between 372 - 1200 nm) was used in combination with an Avantes AvaSpec-ULS2048CL-EVO UV/Vis spectrometer accompanied by OH UV/Vis fibre optic cables (2 m length) to monitor the photo-switches of the films. Later, individual LEDs (365 nm and 455 nm) were purchased from Thorlabs and a UV-Vis-NIR Jasco V-780 spectrometer was used for the cycling tests of the films tested with additional sun exposure between measurements.

Most of the material for the outdoor setup was purchased from BAUHAUS in Spain and included Soprema Sopra XPS SL 100 extruded polystyrene sheets (8 sheets with dimensions: L x W x H 125 x 60 x 10 cm), Placo Saint-Gobain Gypsum plasterboard BA 10 (4 sheets with dimensions: L x W x H 250 x 120 x 10 cm), reflective material (emergency blanket), 30 cm x 2 cm in diameter plastic pipe (for the cables of each instrument), white aluminum pieces for the frame of the box (L x W x H 2,600 x 15 x 15 mm), weather proof box for storing instruments, power cable and extension cord, powersplit multiple socket outlet, EUROKRAFTpro assembly trolley for placement of the model. A PROXXON 2227080 styrofoam cutting device was used to cut the polystyrene sheets. A HOBO 4-channel thermocouple logger and 4 copper wire thermocouples (T-type) were used for the temperature measurements. Additionally, a fibre optic cable splitter and laptop were used together with the Avantes spectrometer to monitor the photo-switches of the MOST-materials in the model house.

Avantes software AvaSoft 8.11 Basic was used for the data acquisition of the spectroscopy measurements and HOBOWare software was used in combination with the HOBO temperature logger. The data acquired was processed using Python and Excel.

3.2 Experimental Procedures

The experimental procedures are divided into two parts; small scale experiments and construction and monitoring of the outdoor setup. Below are the in depth procedures of each part.

3.2.1 Determining Extinction Coefficients

By determining the extinction coefficient of the various photoswitching molecules and using a set film thickness of 20 μm , the required concentration of each respective MOST-molecule in order to achieve a desired absorbance could be determined. The extinction coefficient for NBD4c (18 200 000 $\text{cm}^2\text{mol}^{-1}$) and NBD4b (8 200 000 $\text{cm}^2\text{mol}^{-1}$) were previously known from literature. In order to calculate the extinction coefficients of the ANKS and DHA, a serial dilution was carried out. First, 5 mg of each molecule was diluted with 25 mL toluene. Then 1 mL of the solution was

placed in a separate vial and diluted with toluene to a total volume of 25 mL ("Dilute 1"). Finally, 5 mL of the second solution was extracted and diluted again with toluene to 25 mL ("Dilute 2"). UV/Vis measurements of the two last solutions were performed and the average extinction factor of the two solutions was determined via Lambert Beer's law. The values of the extinction coefficients from each serial dilution of the photo-switches can be observed in Table 3.1 and the average was used to calculate the amount of molecule needed to achieve a desired absorbance of the films.

Table 3.1: Extinction coefficients.

| Molecule | Dilute 1 [cm ² mol ⁻¹] | Dilute 2 [cm ² mol ⁻¹] | Average extinction coeff. [cm ² mol ⁻¹] |
|----------|--|--|---|
| ANK240 | 18 036 385 | 17 571 691 | 17 804 038 |
| ANK241 | 13 364 574 | 13 197 965 | 13 281 270 |
| ANK242 | 18 308 561 | 18 051 616 | 18 180 089 |
| DHA | 6 491 536 | 6 408 704 | 6 450 120 |

3.2.2 Blade Coating of PMMA Substrates

The PMMA substrates (L x W x H: 75 x 25 x 2 mm) were first cleaned by adding them to a bath of Hellmanex soap solution for 5 minutes, then rinsed with deionised water, dried using high pressure air and after added to another bath containing isopropanol 99.9% for 5 minutes. The substrates were rinsed and dried once again. In the final cleaning step, the PMMA substrates were placed in an ozoner cleaner for 1 minute.

Polystyrene/toluene solutions with $c = 200 \text{ g L}^{-1}$ were prepared by mixing 0.40 g polystyrene (PS) pellets with 2 mL toluene in small vials with a magnetic stirring bar. Toluene was chosen as the solvent since it has a similar dielectric constant as polystyrene (both molecular structures have a benzene ring and an alkyl group). The vials were placed on a hot plate at 65 °C and mixed for a duration of 3 hours to achieve a homogeneous solution.

For the initial tests of the blade coater, only a solution of polystyrene was coated on to the PMMA substrates, and the film thicknesses were recorded as a function of coating speed. Later, for coating of the photochromic films, a set amount of MOST-molecules was added to the PS solutions which was based on achieving a 20 µm thick film as well as a desired absorbance (specified in Tables 3.2, 3.3 and 3.4). Due to degradation of the molecules in solution over time, 1 - 3 different vials were prepared for each respective photoswitch and the amounts determined by the extinction factors as well as the resulting concentrations of each solution are presented in Table 3.2, Table 3.3 and Table 3.4.

3. Methods

Table 3.2: Concentration of MOST-molecules based on calculated extinction coefficients in vial 1.

| Molecule | Theor. abs [a.u.] | Theor. mass [mg] | Weighed mass [mg] | Conc. [mol cm ⁻³] |
|----------|----------------------|---------------------|----------------------|----------------------------------|
| NBD4c | 0.2 | 4.02 | 4.2 | 5.73 x 10 ⁻⁶ |
| NBD4b | 0.2 | 4.27 | 4.5 | 6.36 x 10 ⁻⁶ |
| ANK240 | 0.2 | 2.85 | 2.9 | 5.68 x 10 ⁻⁶ |
| ANK241 | 0.2 | 4.37 | 4.6 | 7.17 x 10 ⁻⁶ |
| ANK242 | 0.2 | 2.22 | 2.5 | 5.57 x 10 ⁻⁶ |
| DHA | 0.1 | 4.33 | 4.9 | 1.57 x 10 ⁻⁵ |

Table 3.3: Concentration of MOST-molecules based on calculated extinction coefficients in vial 2.

| Molecule | Theor. abs [a.u.] | Theor. mass [mg] | Weighed mass [mg] | Conc. [mol cm ⁻³] |
|----------|----------------------|---------------------|----------------------|----------------------------------|
| NBD4c | 0.2 | 4.02 | 4.0 | 5.46 x 10 ⁻⁶ |
| NBD4b | - | - | - | |
| ANK240 | 0.2 | 2.85 | 3.2 | 6.25 x 10 ⁻⁶ |
| ANK241 | 0.2 | 4.37 | 5.1 | 7.95 x 10 ⁻⁶ |
| ANK242 | 0.2 | 2.22 | 2.5 | 5.52 x 10 ⁻⁶ |
| DHA | - | - | - | |

Table 3.4: Concentration of MOST-molecules based on calculated extinction coefficients in vial 3.

| Molecule | Theor. abs [a.u.] | Theor. mass [mg] | Weighed mass [mg] | Conc. [mol cm ⁻³] |
|----------|----------------------|---------------------|----------------------|----------------------------------|
| NBD4c | 0.2 | 4.02 | 4.0 | 5.60 x 10 ⁻⁶ |
| NBD4b | - | - | - | |
| ANK240 | 0.2 | 2.85 | 3.2 | 5.68 x 10 ⁻⁶ |
| ANK241 | - | - | - | |
| ANK242 | - | - | - | |
| DHA | - | - | - | |

The temperature of the blade coater was set to 60°C and the clean PMMA substrates were placed on the hot plate for approximately 20 minutes for heating. The desired film thickness of the coatings was chosen to be 20 µm and the height of the blade was fixed at 25 µm. In order to test the blade coater, the speed of the blade coater was adjusted between 1 and 60 mm s⁻¹ and the achieved film thicknesses were monitored with a micrometer instrument. 100 µL polystyrene solution was placed at the base

of the PMMA substrates and the blade was allowed to move over the panels to coat them. The achieved thicknesses of the films, as well as all other parameters, are presented below in *Results*.

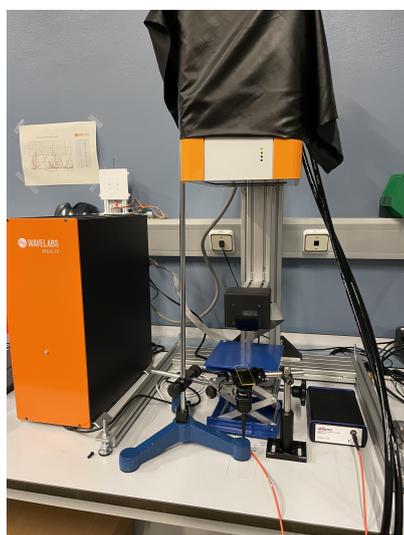
Cleaning and blade coating of the larger PMMA substrates (L x W x H 175 x 75 x 2 mm) in order to fabricate the windows for the outdoor setup were performed under similar conditions as for the smaller substrates. Based on the discoveries of the small scale tests, NBD4c and ANK240 were selected to study on the larger scale. Two separate solutions containing NBD4c/PS and ANK240/PS were prepared based on a desired wt% MOST-molecule of 0.5 %. The amounts are summarised in Table 3.5. A volume of 1000 μL polymer solution was placed at the base of the larger substrates and coated at $T = 60\text{ }^{\circ}\text{C}$ and a speed of 5 mm s^{-1} . The film thicknesses were measured with a handheld micrometer. Coating results are presented in *Results*.

Table 3.5: Amount of MOST-molecules based on desired wt% in PS solutions for coating of large PMMA substrates.

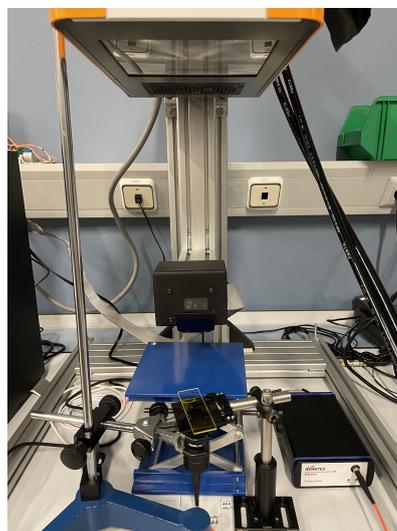
| Molecule | Theor. abs [a.u.] | Theor. mass [mg] | Weighed mass [mg] | wt%. [%] |
|----------|----------------------|---------------------|----------------------|-------------|
| NBD4c | 0.2 | 10.0 | 10.3 | 0.51 |
| ANK240 | 0.2 | 11.0 | 11.1 | 0.54 |

3.2.3 LED Exposure and Cycling Measurements

Initially, the setup for the LED exposure of the coated PMMA substrates consisted of the Wavelabs SINUS-70 solar simulator and simultaneous monitoring of the photo-switches with the Avantes spectrometer using fibre optic cables pointed perpendicular toward the substrates as well as the LEDs. The resulting raw spectra from the spectrometer shows transmittance (in counts) as a function of wavelength. In Figure 3.1 the samples were placed over the optical diffuser (see Figure 3.1).



(a) Wavelabs SINUS-70 Solar Simulator.



(b) Placement of sample with fibre optic cable directed perpendicular to the sample and light source.

Figure 3.1: Set up of small scale UV/Vis measurements using the solar simulator together with the Avantes spectrometer.

The LEDs used in the SINUS-70 solar simulator were selected according to the individual absorbance maxima of the different photo-switches (see Table 3.6). The NBD4c films were exposed to all wavelengths in the range of 372 nm to 700 nm and the ANK film were only exposed to the 372 nm LED. The spectra of the LED wavelengths used in the solar simulator for irradiating the films are shown below in Figure 3.2 where the y-axis is in counts.

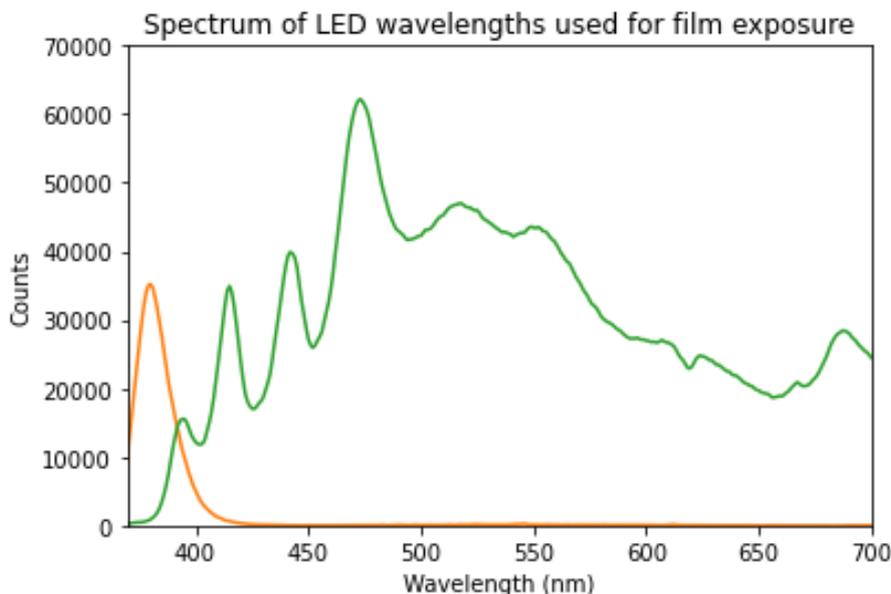


Figure 3.2: Spectrum of LED wavelengths used for irradiation of the NBD and ANK films.

The full LED spectrum (green spectrum) was not used to irradiate the ANK films due to the high intensities of the LEDs above the absorbance maximum of the ANKs meaning that the LED at 372 nm (orange spectrum) was comparatively not intense enough to induce noticeable photo-switches of the ANKs. For this reason, the ANK films were only irradiated with the LED at 372 nm which meant that it was able to achieve higher counts. Note that the intensity of the LED at 372 nm was however still equivalent to the intensity of the specific wavelength of one sun (30 %). Additionally, due to the light emitted from the LEDs being very saturated in the spectrometer, an optical diffuser as well as a polarising film was used to lower the saturation of the measurements.

The cyclability of the films was measured to follow the absorbance of the materials over time. The various photo-switches were loaded into PS at two different concentrations each and with two different film thicknesses (specified in *Results*). The cyclability tests were performed by exposing the films to LED light once daily for 5 consecutive days and determining the maximum and minimum absorbance prior and post exposure respectively. Prior to exposure, a reference spectrum of a clean PMMA substrate was taken as a baseline. During exposure of the films a measurement was recorded once every 150 ms (NBD) or once every 2 seconds (ANKs) with the spectrometer and UV/Vis spectra were created in Python to visualise the photoswitch. Table 3.6 shows the parameters of the LED exposure using the solar simulator for the various photo-switches.

3. Methods

Table 3.6: LED exposure and measurement parameters.

| Molecule | Abs max [nm] | LED wavelength [nm] | Intensity [%] | Expose time [s] | Interval [ms] |
|----------|-----------------|------------------------|------------------|--------------------|------------------|
| NBD4c | 450 | 372 - 700 | 100 | 20 | 150 |
| ANK240 | 379 | 372 | 30 | 120 | 2000 |
| ANK241 | 382 | 372 | 30 | 120 | 2000 |
| ANK242 | 364 | 372 | 30 | 120 | 2000 |

The cyclability of photo-switches NBD4c and ANK240 were additionally tested by exposing them to the sun between LED exposure measurements. Prior to initial sun exposure, new films were prepared and irradiated with individual LED wavelengths for set intervals (from 5 up to 120 seconds) until they had completely photo-switched, i.e. the absorbance was close to 0 (see setup in Figure 3.3).

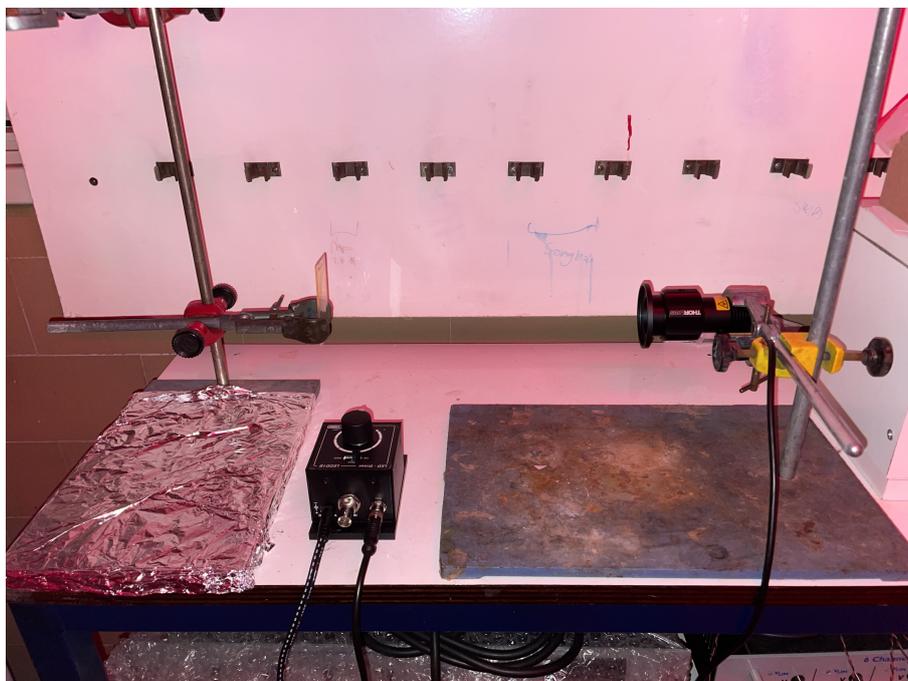


Figure 3.3: Setup of exposure with individual LEDs.

Exposure was performed in a dark room to eliminate impact of other light. A reference spectrum of a clean PMMA substrate was measured prior to exposure measurements. After each exposure the absorbance was measured using a UV-Vis-NIR Jasco V-780 spectrometer. All spectroscopic measurements were performed by attaching the substrates to a sample holder, which ensured the measurements were made at the exact same spot of the sample, scanning the wavelength from 700 to 190 nm. Later, the films were placed outside in sunlight during the day and overnight (roughly 16 hours) and then put in the dark for 2 - 3 hours before LED irradiation and UV/Vis measurements. The changes in absorbance of the films were monitored

daily for a period of 5 days. Table 3.7 shows the parameters of the cyclability tests of the NBD4c and ANK240 films with additional sun exposure.

Table 3.7: Parameters for cyclability tests with sun exposure.

| Molecule | LED wavelength [nm] | Total LED exposure time [s] | # of cycle days [d] |
|----------|------------------------|--------------------------------|------------------------|
| NBD4c | 455 | 100 | 5 |
| ANK240 | 365 | 240 | 5 |

3.2.4 Construction and Monitoring of the Outdoor Setup

The outdoor setup was constructed and located on the roof of the Institute of Materials Science of Barcelona (ICMAB-CSIC), where daily monitoring was performed. The setup was directed 180° south with the sample window toward the east and the reference toward the west. The construction process consisted of cutting the plaster and styrofoam into individual pieces with the desired dimensions.

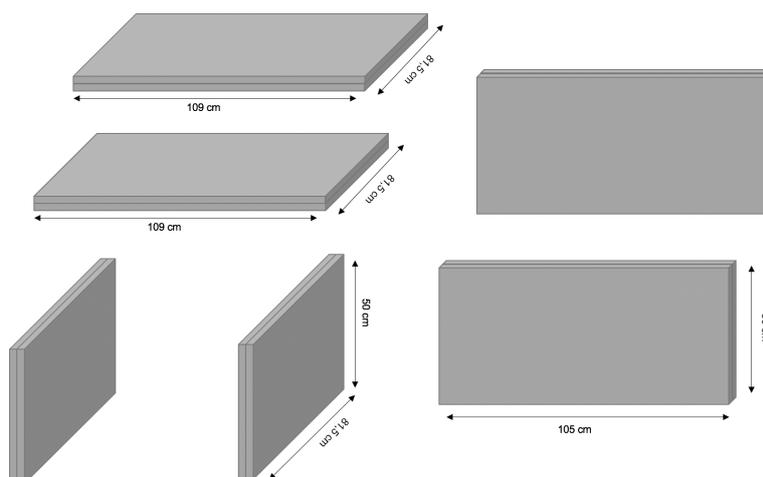


Figure 3.4: Dimensions of plaster pieces (not scaled).

Figure 3.4 shows the pieces of plaster with dimensions. Each plaster component was 1 cm thick and placing two of them together created 2 cm thick pieces which were assembled over the styrofoam. The individual 10 cm styrofoam blocks were cut to the specific pieces with dimensions shown in Figure 3.5. In reality, 0.5 cm was removed from the length of each styrofoam piece in order to create a margin for the assembly of the house. Placing the 10 cm thick pieces together created a 30 cm thick insulation on each side and between the cavities of the box.

The styrofoam and cast material were placed and held together by an aluminium frame (same lengths as the pieces of plaster) which was screwed to the sides of the house as reinforcement. The house was covered in a reflective material (equivalent to an emergency blanket) in order to minimise heating of the house through convection

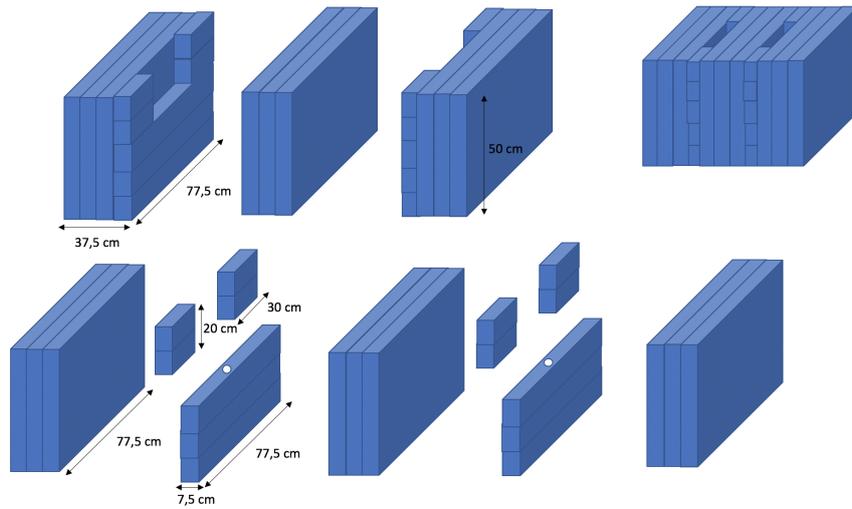


Figure 3.5: Dimensions of styrofoam pieces (not scaled).

of the walls. Finally, a wooden frame was attached to the bottom to lift the house so that cables were able to run through and to the monitoring instruments. In order to be able to thread the thermocouples and fibre optic cables to the cavities, two 2 cm in diameter holes are created in the plaster and bottom pieces of styrofoam. The UV/Vis spectrometer, temperature logger and laptop were placed on the outside of the model house in a separate weather proof box.

The indoor and outdoor temperatures of each "room" were monitored using four different thermocouples which were attached to the outside of the box and placed on the surface of the windows, as well as thread through the box and placed in the centre of each box. Additionally, the outdoor temperature on the roof of the ICMAB building was monitored as a reference. The fibre optic cables were also thread through the box and arranged perpendicular toward the window at roughly a 5 cm distance. The temperature was monitored over a 4 day period and later plotted in a diagram for comparison between the reference and sample windows.

4

Results and Discussion

The aim of this thesis project was to test the MOST-molecules (NBDs, ANKs, and DHAs) in polystyrene (PS) coatings on small scale PMMA substrates, to analyse the photo-switches based on film thickness and concentration and compare them to each other. Based on the discoveries, photo-switch ANK240 was selected for testing on a larger scale. In this section, the results from the small scale tests as well as from the outdoor set up are presented and discussed.

4.1 Blade Coating Tests

Initial runs of the blade coater were performed for the purpose of monitoring film thickness as a function of blade coating speed. Firstly, various parameters were altered such as the polystyrene (PS) concentration, the volume of PS solution applied to the substrate and the temperature. After several test runs, the desired viscosity of PS solution was achieved at 200 g L^{-1} and the volume to cover the small PMMA substrates was fixed at $100 \text{ }\mu\text{L}$.

At first the temperature was set to $80 \text{ }^\circ\text{C}$ based on toluene, but later was decreased to $60 \text{ }^\circ\text{C}$ since the solvent evaporated too rapidly and the PS solution was not evenly distributed over the substrate. Lastly, the speed of the blade varied between $1 - 60 \text{ mm s}^{-1}$. The blade coating parameters and achieved film thicknesses have been summarised in Table 4.1.

Table 4.1: Blade coating parameters and achieved film thicknesses.

| PS concentration [g L^{-1}] | Volume PS solution [μL] | Speed [mm s^{-1}] | Temp. [$^\circ\text{C}$] | Film thickness [μm] |
|---|---|---------------------------------|-------------------------------|-------------------------------------|
| 200 | 100 | 1 | 60 | 20.6 |
| 200 | 100 | 2 | 60 | 19.2 |
| 200 | 100 | 5 | 60 | 15.5 |
| 200 | 100 | 10 | 60 | 12.0 |
| 200 | 100 | 15 | 60 | 22.3 |
| 200 | 100 | 30 | 60 | 23.2 |
| 200 | 100 | 60 | 60 | 22.3 |

An important observation of the films were that they adhered well to the PMMA

substrates and did not at any point peel off. From Table 4.1 it is shown that the film thickness gradually decreases as the blade speed is increased to a point where it turns and increases again at higher speeds, as well as the difference in film thickness between 5 and 10 mm s^{-1} and 10 and 15 mm s^{-1} is relatively high. What should also be noted is although the speed from 15 mm s^{-1} is doubled to 30 and after 60 mm s^{-1} , the film thicknesses remain similar values. The coating results as a function of coating speed can be interpreted more intuitively in 4.1 below.

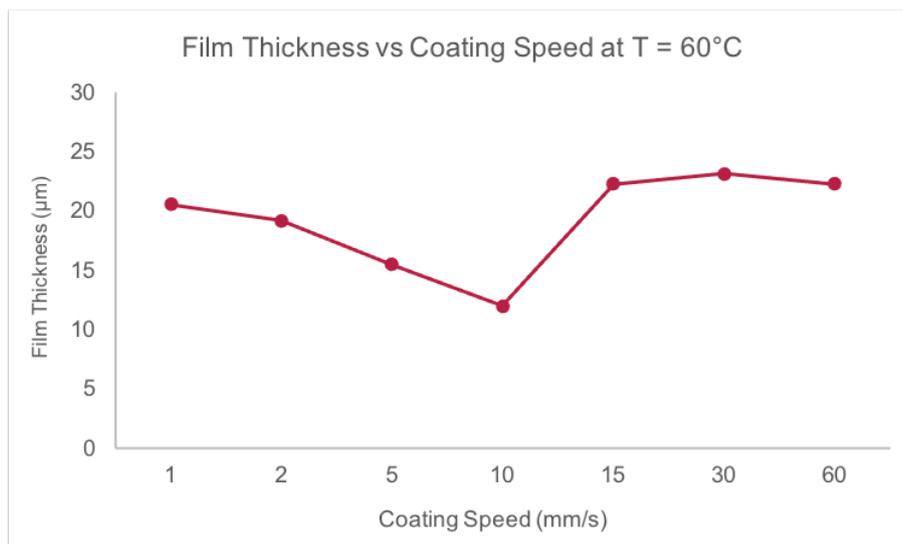


Figure 4.1: Film thickness as a function of blade coating speed.

What can be interpreted visually from Figure 4.1 is that the graph acquires a "V" shape as the thickness slowly decreases with coating speed until it reaches a point and the trend changes upward again with higher speeds. Although it may seem as though higher velocities achieve desirable thicknesses, what is not shown in Table 4.1 nor Figure 4.1 is the visual coating result. What was noted optically was that at speeds of 1, 2 and 5 the films were homogeneous, even and covered the entire substrate mm s^{-1} . At 10 mm s^{-1} the coatings were homogeneous and covered the entire substrate but acquired a gradient profile. At higher velocities, the films were comparably thicker and only covered a small portion of the substrate. This could be due to the blade moving too quickly for the solution to be evenly distributed over the PMMA.

An idea of achieving more desirable coating results at high blade speeds was to increase the amount of PS solution applied to the substrate from 100 to 120 μL . This however did not make much of a difference in uniformity of the film since the excess volume of solution did not manage to cover the substrate and was instead "pushed" to the other end.

Later, the various MOST-molecules were introduced to the polystyrene solutions respectively. Below are the parameters and achieved film thicknesses of each photo switch sample. What should be noted is that the MOST concentration differs between the samples since various batches of solution were prepared. This was due to a noticeable degradation of the molecule in the PS solution over time.

4.2 Small Scale Exposure and Cycling Measurements

After the blade coatings tests, the MOST-molecules were incorporated in viscous polystyrene solutions and coated on to small PMMA substrates. Here the concentration of molecule was dependent on the extinction coefficient as well as the desired absorbance of the film. For detecting significant changes in the indoor environment of the model house, an absorbance of $A = 2$ is appropriate and calculations of amounts and concentrations were therefore based on this value. However, due to limitations in the amount of MOST-molecules available for the experiments, the concentrations were scaled down by a factor of 10 and the expected absorbance was consequently $A = 0.2$. It is important to note this aspect as the results may only give an indication of how the systems will work.

The objectives of the small scale tests were to establish how film thickness and concentration of the coatings impact on the photo-switches of the MOST-molecules and to compare the photo-switches of the various MOST-molecules incorporated in polymer matrices. Below is an overview of the discoveries.

4.2.1 Coating and Exposure of Photo-switch NBD4c

Photo-switch NBD4c was selected for testing in films since changes in the absorbance maximum at 454 nm were more easily detectable in the solar spectrum compared to NBD4b at 374 nm due to the intensity of wavelengths between 400 - 450 nm being significantly higher. Solutions of photo-switch NBD4c and polystyrene were prepared and coated on to small PMMA substrates. Later, two samples with different film thicknesses were irradiated once hourly for a period of 5 hours and two other samples were irradiated once daily for a period of 5 days. In Table 4.2 the parameters and results of the blade coating of photo-switch NBD4c are presented.

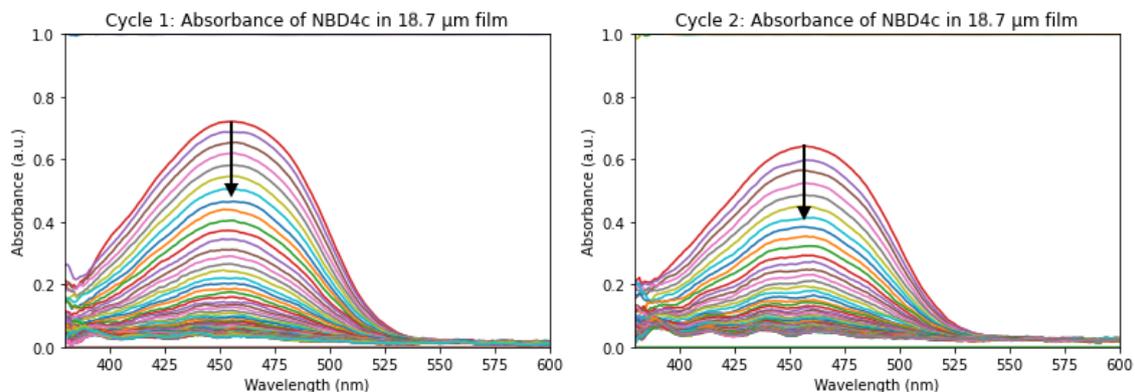
Table 4.2: Blade coating parameters and results for NBD4c.

| Sample # | Speed [mm s ⁻¹] | NBD conc. [mol cm ⁻³] | Film thickness [μm] |
|----------|--------------------------------|--------------------------------------|------------------------|
| 0 | 2 | 5.73 x 10 ⁻⁶ | 18.7 |
| 2 | 5 | 5.73 x 10 ⁻⁶ | 19.6 |
| 4 | 2 | 5.46 x 10 ⁻⁶ | 21.7 |
| 5 | 5 | 5.46 x 10 ⁻⁶ | 23.9 |
| 7 | 5 | 5.60 x 10 ⁻⁶ | 20.1 |

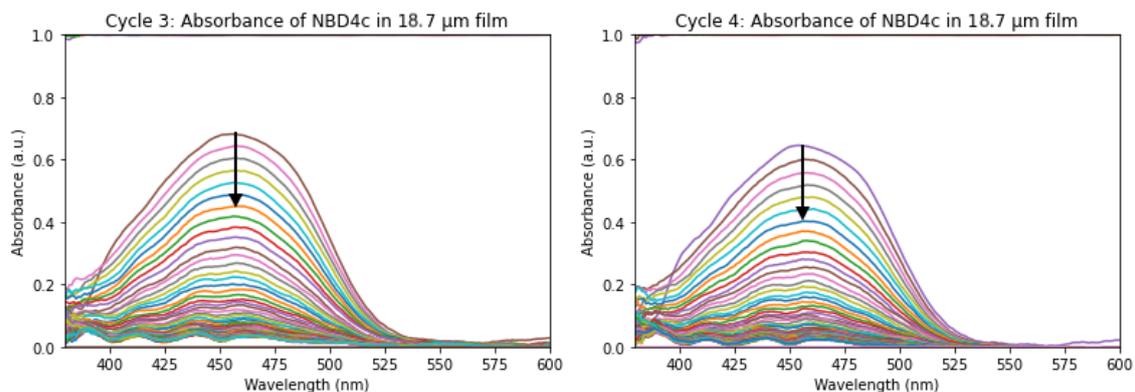
The reason for the difference in NBD concentrations between the various samples was due to the degradation of the molecules in polystyrene after a period of time (2 - 3 weeks) which meant that new solutions had to be prepared. Samples 4 and 5 were exposed to LED irradiation (372 - 700 nm) for a duration of 20 seconds once hourly for 5 consecutive hours, whilst samples 0 and 2 were exposed once daily for 5

4. Results and Discussion

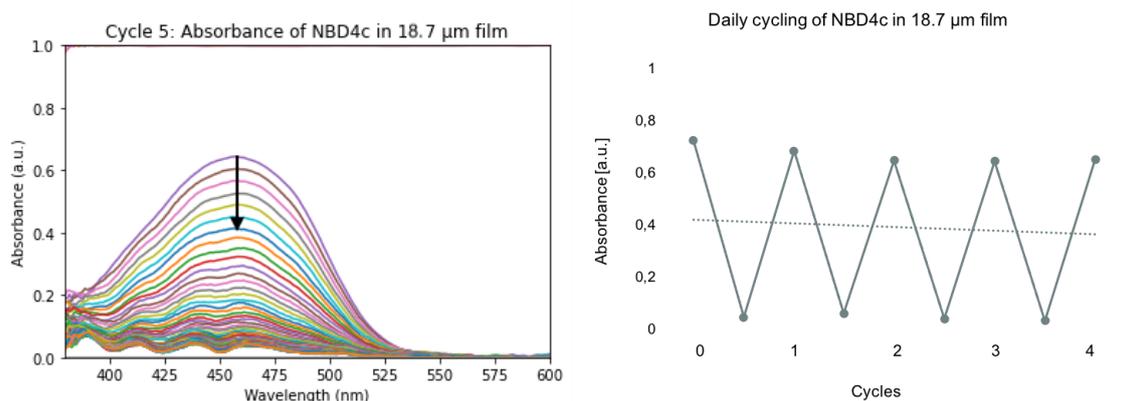
days. Below, UV/Vis spectra of sample 0 are presented in Figure 4.2 as an example of the cycling tests. Results from the other samples are shown in Appendix 1.



(a) Photo-switching cycle 1 of NBD4c in 18.7 μm film. (b) Photo-switching cycle 2 of NBD4c in 18.7 μm film.



(c) Photo-switching cycle 3 of NBD4c in 18.7 μm film. (d) Photo-switching cycle 4 of NBD4c in 18.7 μm film.



(e) Photo-switching cycle 5 of NBD4c in 18.7 μm film. (f) Cycle analysis of a) - e) showing 0.46% decrease in absorbance.

Figure 4.2: UV/Vis spectra and cycling analysis of daily cycles of photo-switch NBD4c in an 18.7 μm film when exposed to LED wavelengths between 372 - 700 nm once daily for 20 seconds and placed in the dark between measurements.

What is shown in sub figures a) - e) in Figure 4.2 is the change in absorbance of photo-switch NBD4c in an 18.7 μm film (sample 0) when being exposed to LED irradiation for a duration of 20 seconds in a range of 372 - 700 nm. The irradiation measurements were carried out once daily for a period of 5 days and the film was placed in the dark between measurements. The spectra were created by dividing the transmittance with the reference and then plotting it logarithmically according to Equation 2.2 in section *Theory* to achieve absorbance on the y-axis.

The result of the cycling analysis showed an average decrease in absorption of 0.46% over the cycles. This may give an indication that photo-switch NBD4c becomes slightly less efficient at storing energy over time in a polystyrene film. Although, this would still mean that the recovery of the film between cycles is on average around 99.5%.

However, what should also be noted is some of the uncertainties connected to these measurements. Between each cycle, the sample was placed at a constant distance from the LEDs as well as from the fiber optic, however it is difficult to place the sample so that the exact same part of the film is exposed each time. This is partly shown by the distance of the final absorption curve and absorbance 0, which indicates the reflection of the sample. One reason for the differences between the cycles may be the thickness of the film varying slightly over the substrate causing differences in reflection of the PMMA. For example in Figure 4.2c, there seems to be a higher reflectance from the substrate than compared to Figure 4.2e. This may affect the overall spectrum and lead to a higher initial and final absorbance.

Due to the uncertainty of the measurements using the LED simulator, new cycling measurements were performed on sample 7, but with a different setup. As described in section *Experimental Procedures* an individual LED (455 nm) was used to irradiate the sample for 5 - 100 seconds in total. The changes in absorbance were monitored using the JASCO spectrometer together with a film holder, ensuring the measurements were made at the exact same spot of the sample. After the measurements, the sample was placed in the sun for 6 hours and then in the dark and again irradiated the same way the following day for 5 consecutive days. The resulting UV/Vis spectra from the experiment of a 20.1 μm film (sample 7) are shown below in Figure 4.3.

4. Results and Discussion

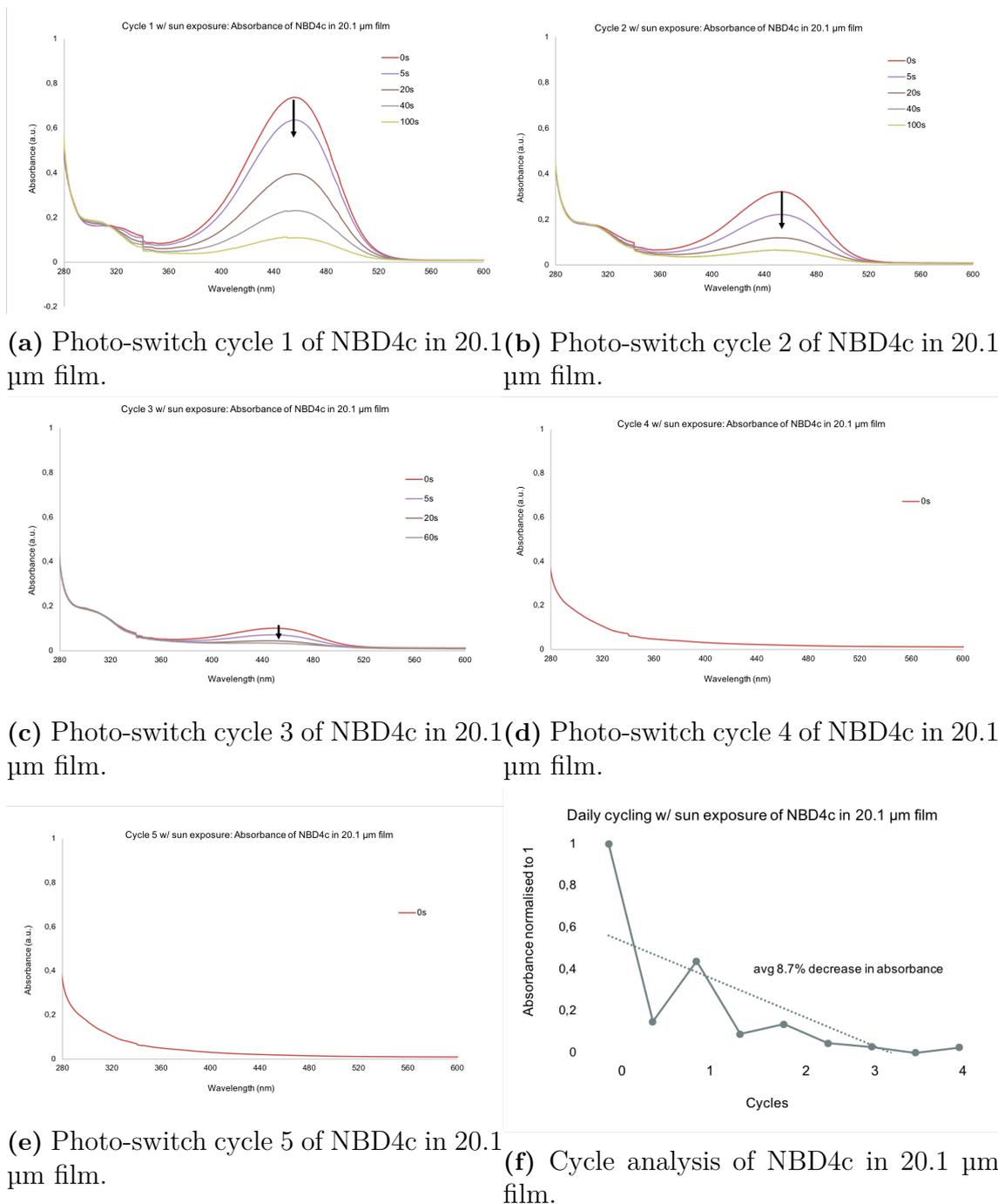


Figure 4.3: UV/Vis spectra and cycling analysis of daily cycles of photo-switch NBD4c in a 20.1 μm film when exposed to 455 nm LED wavelength (0 - 100 s in total) during 5 days and placed in the sun for 6 hours and later in the dark between each measurement. Each spectrum curve represents the measured absorbance after irradiation.

Compared to the cycling tests of sample 0 without sun exposure, it is clear that for sample 7 there seems to be a large effect of the sun on the film. At each measurement the absorbance decreases significantly until it reaches 0 after 3 days.

The trend is shown in the cycling analysis where the absorbance decreases 8.7% on average, however regardless of this number the film does not ever recover between cycles as compared to sample 0. This may have to do with the indicated half-life of NBD4c in solution of 0.64 h, making it unsuitable in films for window applications.

4.2.2 Coating and Exposure of Photo-switch ANK240

Azothiophenes have according to literature shown promising potential for MOST-applications and although the same thing can be said about the absorbance maximum of the ANK molecules as of NBD4b mentioned above (each are between 360 - 380 nm), they remained of value to study in this thesis project. Three of the samples with different film thicknesses were chosen for the exposure measurements as indicated in 4.3.

Table 4.3: Blade coating parameters and coating results for photo-switch ANK240.

| Sample # | Speed [mm s ⁻¹] | Film thickness [μm] | ANK conc. [g cm ⁻³] |
|----------|--------------------------------|------------------------|------------------------------------|
| 5 | 2 | 15.7 | 5.68 x 10 ⁻⁶ |
| 6 | 5 | 16.4 | 5.68 x 10 ⁻⁶ |
| 13 | 5 | 20.5 | 6.26 x 10 ⁻⁶ |

Sample 5 and 6 were chosen to study in the same way (with an identical setup) as sample 0 and 2 of the NBD4c photo-switch. However the films were irradiated with only a 372 nm wavelength from the LED simulator and the full range of LEDs. The reason was due to the low intensity of this specific wavelength in the full LED spectrum which was not able to induce a photo-switch of the azobenzenes. This is explained further in *LED Exposure and Cycling Measurements in Methods*. When dividing the raw transmittance spectra from the spectrometer with the reference to get the absorbance of the films, only a small range of wavelengths are shown. As a result, the UV/Vis spectra appear differently compared to the NBD4c as shown in Figure 4.4.

4. Results and Discussion

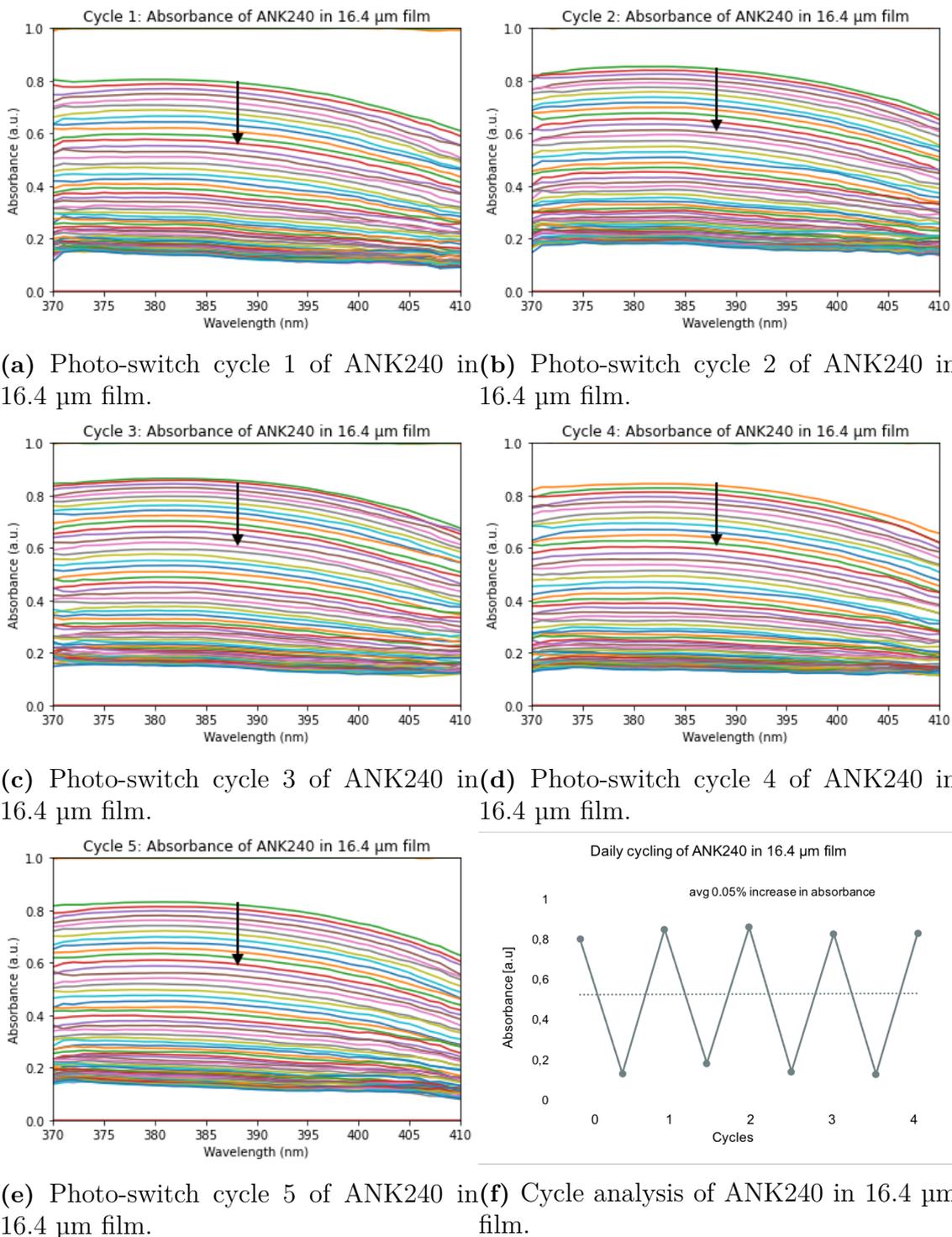


Figure 4.4: UV/Vis spectra and cycling analysis of daily cycles of photo-switch ANK240 in a 16.4 μm film when exposed to 372 nm LED wavelength (2 minutes) and placed in the sun for 6 hours and after in the dark between measurements.

The ANK240 film was exposed for 2 minutes with a 372 nm LED from the solar simulator and from the spectra shown above in Figure 4.4 it is visible that the reflection from the PMMA is higher compared to the NBD4c samples (the distance

between absorbance 0 and the lowest measured absorbance of the sample). This would suggest that the measured absorbances are also higher than in reality. From Figure 4.4f it is shown that the absorbance of the film increases by an average of 0.05% over the cycles.

4. Results and Discussion

Additionally, sample 13 was tested the same way as sample 7 of the NBD4c photo-switch by irradiating with an individual LED (365 nm) and then placed in the sun for 6 hours each day between measurements. The resulting spectra are shown below in Figure 4.5.

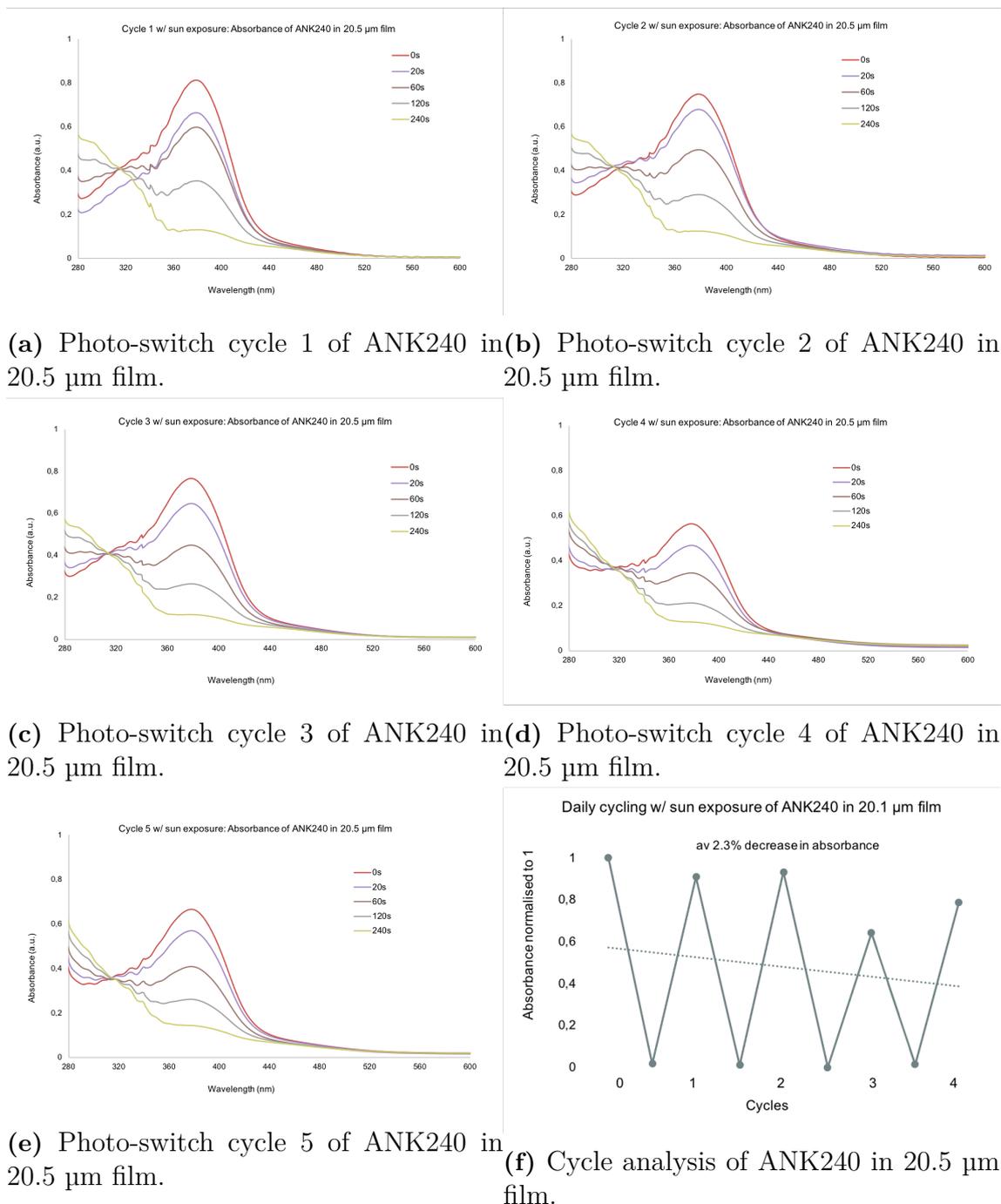


Figure 4.5: UV/Vis spectra and cycling analysis of daily cycles of photo-switch ANK240 in a 20.5 μm film when exposed to 365 nm LED wavelength (0 - 240s in total) during 5 days and placed in the sun for 6 hours and later in the dark between each measurement.

Here it is clear that between each cycle a) - e) the ANK240 film retains a more constant absorbance profile compared to the NBD4c film shown in Figure 4.3. The absorbance decreases on average by 2.3% over the cycles and the film recovery is relatively high compared to the NBD4c. This would suggest that the ANK240 is more stable when being exposed to natural sunlight and was therefore chosen to study on a larger scale in the outdoor setup.

4.2.3 Comparison of MOST-Molecules

One of the aims of this master's thesis project was to study how film thickness and molecule concentration impact on the photo-switches of the MOST-molecules and how the photo-switches compare to each other. The NBD4c samples shown in Table 4.4 more or less have similar concentrations, however differ in film thickness. Due to the differences in film thickness one can additionally observe changes in average absorbance over the cycling measurements.

Table 4.4: Properties of NBD4c films and average absorbance differences after daily cycling measurements without sun exposure.

| Sample # | Film thickness [μm] | NBD conc. [mol cm^{-3}] | Abs diff % |
|----------|-------------------------------------|---------------------------------------|---------------|
| 0 | 18.7 | 5.73×10^{-6} | - 0.46 |
| 2 | 9.6 | 5.73×10^{-6} | + 0.29 |
| 4 | 21.7 | 5.46×10^{-6} | - 0.72 |
| 5 | 23.9 | 5.46×10^{-6} | - 1.0 |
| 7 | 20.1 | 5.60×10^{-6} | - 8.7 |

Samples 0, 4 and 5 all have similar film thicknesses and show a decrease in absorbance. Sample 2 is almost twice as thin as the other samples and has a positive increase in absorbance over the cycles. Sample 7 was exposed to sun light between irradiation measurements and decreases significantly in absorbance compared to the other samples. The general trend shown in Table 4.4 is that the thicker the film becomes the higher the decrease in absorbance is. These results could suggest that the thicker the film is, the lower the recovery between cycles and the average absorbance decreases. However, the reason for sample 2 increasing in absorbance is unclear. The film thickness is notably thinner compared to the other samples, and this may cause the film to recover quickly.

Sample 7 in Table 4.4 was exposed to sunlight between irradiation measurements and shows a high decrease in absorbance over the cycles. The reason for this is when the film is placed in the sun, the photo-switching process occurs constantly back and forth causing the molecules to eventually become less efficient and absorbing and storing energy. This leads to a degradation of the molecule in the film and the absorbance decreases over time.

As for the ANK240 samples shown in Table 4.3, a similar trend dependant on the

thickness of the film is observed. The thinner films (sample 5 and 6) increase in absorbance over the cycles and the thicker film (sample 13) decreases. However, sample 6 only increases slightly compared to sample 5. This may be because the film thickness is somewhere in between that of the thicker and thinner films. Sample 13 was exposed to sunlight between irradiation measurements, however does not decrease as significantly in absorbance as sample 7 of the NBD4c which could suggest that it is more stable when being exposed to natural sunlight.

Table 4.5: Properties of ANK240 films and average absorbance differences after cycling measurements without sun exposure.

| Sample # | Film thickness [μm] | ANK conc. [g cm^{-3}] | Abs diff % |
|----------|-------------------------------------|-------------------------------------|---------------|
| 5 | 9.7 | 5.68×10^{-6} | + 0.69 |
| 6 | 16.4 | 5.68×10^{-6} | + 0.05 |
| 13 | 20.5 | 6.26×10^{-6} | - 2.3 |

Based on these results, the ANK240 photo-switch was chosen to study on a larger scale in the outdoor setup and the results are shown below. UV/Vis spectra and cycling analysis of the other two azobenzenes (ANK241 and ANK242) are shown in Appendix 1.

4.3 Outdoor Measurements

After the small scale testing of the MOST molecules, the outdoor setup was constructed and tested with the ANK240 photo-switch. One of the aims of the larger scale testing was to identify temperature differences of the indoor and outdoor climate of the model house created by the MOST-windows.

Firstly, two plain reference PMMA windows were placed on the openings of the model house to monitor temperature differences between the rooms as a result of the positioning of the house and the direction of the sun. This was performed over 24 hours to observe temperature fluctuations which are shown below in Figure 4.6.

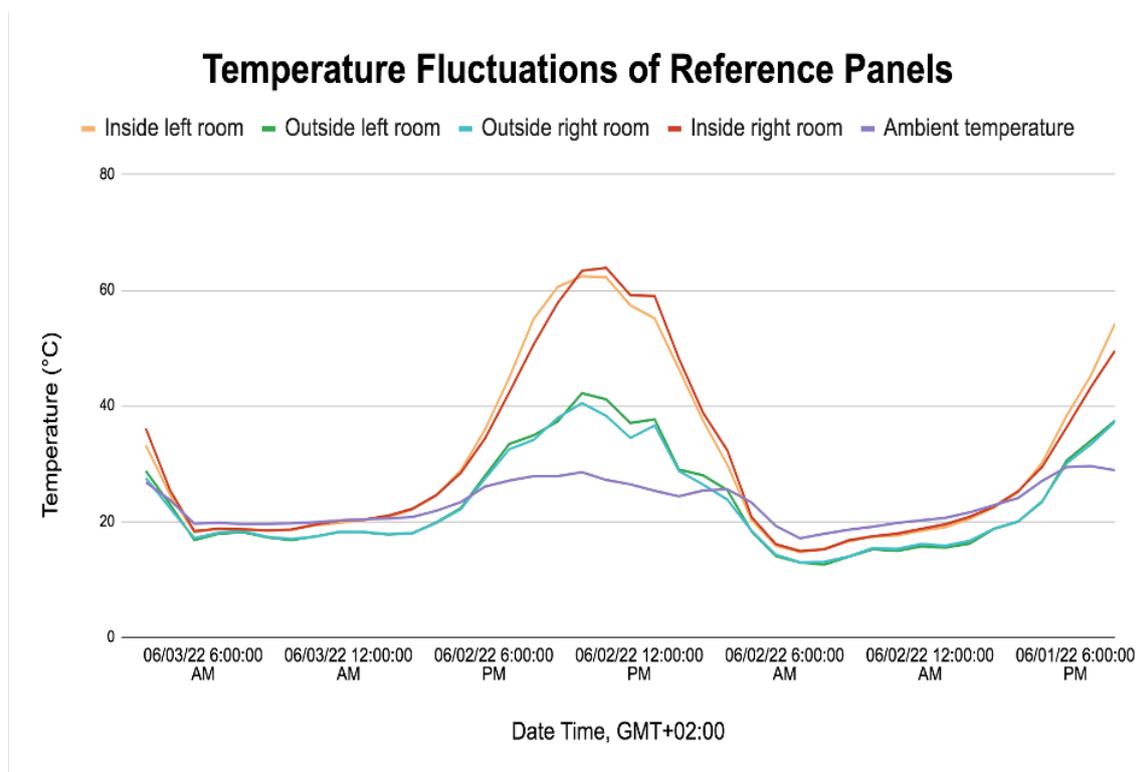


Figure 4.6: Temperature fluctuations over 24 hours of inside and outside rooms of model house with two reference panels.

What is shown in Figure 4.6 is that there is a difference in how the left room and the right room heat and cool over the 24 hours. The left room heats up before the right room which could be explained by the sun rising in the east and therefore hitting the left window first. The right room becomes slightly warmer at the maximum temperature which may be due to the sun shining longer on the right window in the afternoon before it sets in the west. These observations were important to have in mind when later running measurements with the sample window.

Next, the right window was replaced with the sample window coated with a 20.2 μm ANK240 film whilst the left window remained as a reference. The model house was kept facing the same direction as previously and the temperature fluctuations

were monitored over a period of 4 days. The results are shown in Figure 4.7.

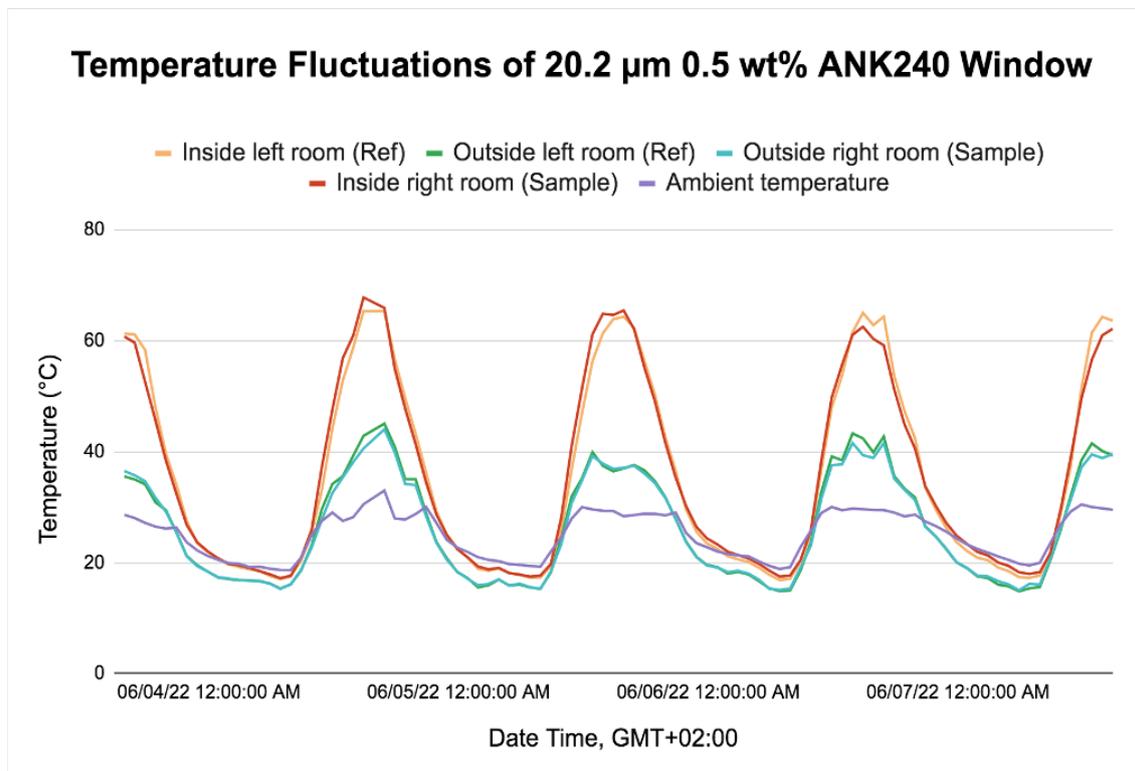


Figure 4.7: Temperature fluctuations over 4 days of inside and outside rooms of model house with ANK240 window.

From the temperature measurements shown in Figure 4.7 it is clear that the inside left room no longer heats up quicker than the inside right room. In fact the right room with the sample window heats up slightly before the left room and reaches a higher maximum temperature. Additionally, both rooms seem to cool down almost simultaneously.

However, what may be a somewhat more important observation is what happens during the night. In the night of the 4th and 5th of June the two rooms have the same temperature, however during the nights of the 6th and 7th of June it is visible that the temperature of the inside right room (with the sample window) is slightly warmer than the inside left room (with the reference window). This may suggest that there is a heat release from the ANK240 window to the interior of the right room. Since the sun has no effect on the photo-switches during the night it is therefore highly likely that this temperature difference is due the heat release from the MOST-molecules.

5

Conclusion

In this Master's thesis the project was divided into two sub-objectives. The first part consisted of small scale testing of the MOST-molecules in polystyrene on small poly(methyl methacrylate) (PMMA) substrates in order to analyse the photo-switches as a function of film thickness and molecule concentration. The second part was to incorporate the MOST-molecules into a larger polystyrene matrix on larger PMMA panels and integrate these panels as windows in a model house exposed to natural solar radiation and monitor the effects of the indoor climate of the house.

The experimental procedure consisted first of blade coating the small scale PMMA substrates with the viscous polystyrene solutions without addition of the MOST-molecules to observe the resulting film thicknesses as a function of coating speed. Once the blade coating parameters were established for achieving the right film thickness, the MOST-molecules were integrated in the coatings and irradiation measurements were carried out in order to observe the behaviour of the photo-switches with respect to molecule concentration and film thickness, and in addition compare them to each other.

The norbornadiene photo-switch NBD4c and azobenzenes ANK240, ANK241 and ANK242 were subjected to LED irradiation in lab both with and without natural solar exposure between measurements, and the absorbance of the films was monitored over a period of 5 days. Comparing the photo-switches which were not exposed to the sun between measurements, the general trend was that the absorbance of the film decreased more notably with increasing film thickness. Additionally, from the small scale tests it was shown that the norbornadiene NBD4c photo-switch degraded remarkably each measurement when being exposed to the sun. However, the ANK240 maintained a similar absorbance spectrum over time and proved therefore to be the more stable candidate for further testing in windows of the model house.

Proceeding to the second part of the project, which consisted of the outdoor setup. The model house was designed in AutoCAD and constructed in order to integrate the MOST-molecules as films on windows. The ANK240 window showed a notable temperature increase during the night of the indoor environment of the model house when compared to the reference window. As the sun has no effect on the photo-switches during the night this would suggest that the MOST-molecules absorb energy from the sun during the day and release it as heat during the night. However, due to the low concentration of molecules in the window, the temperature difference is not that significant.

5. Conclusion

In order to determine the difference in colour of the MOST-materials over time additional UV/Vis measurements must be carried out in the outdoor setup. Further research may also include determining the half-life of the MOST-molecules in polystyrene films on PMMA substrates in order to determine how this property affects the indoor climate of the model house.

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A

Appendix 1

A.1 UV/Vis Spectra of NBD4c

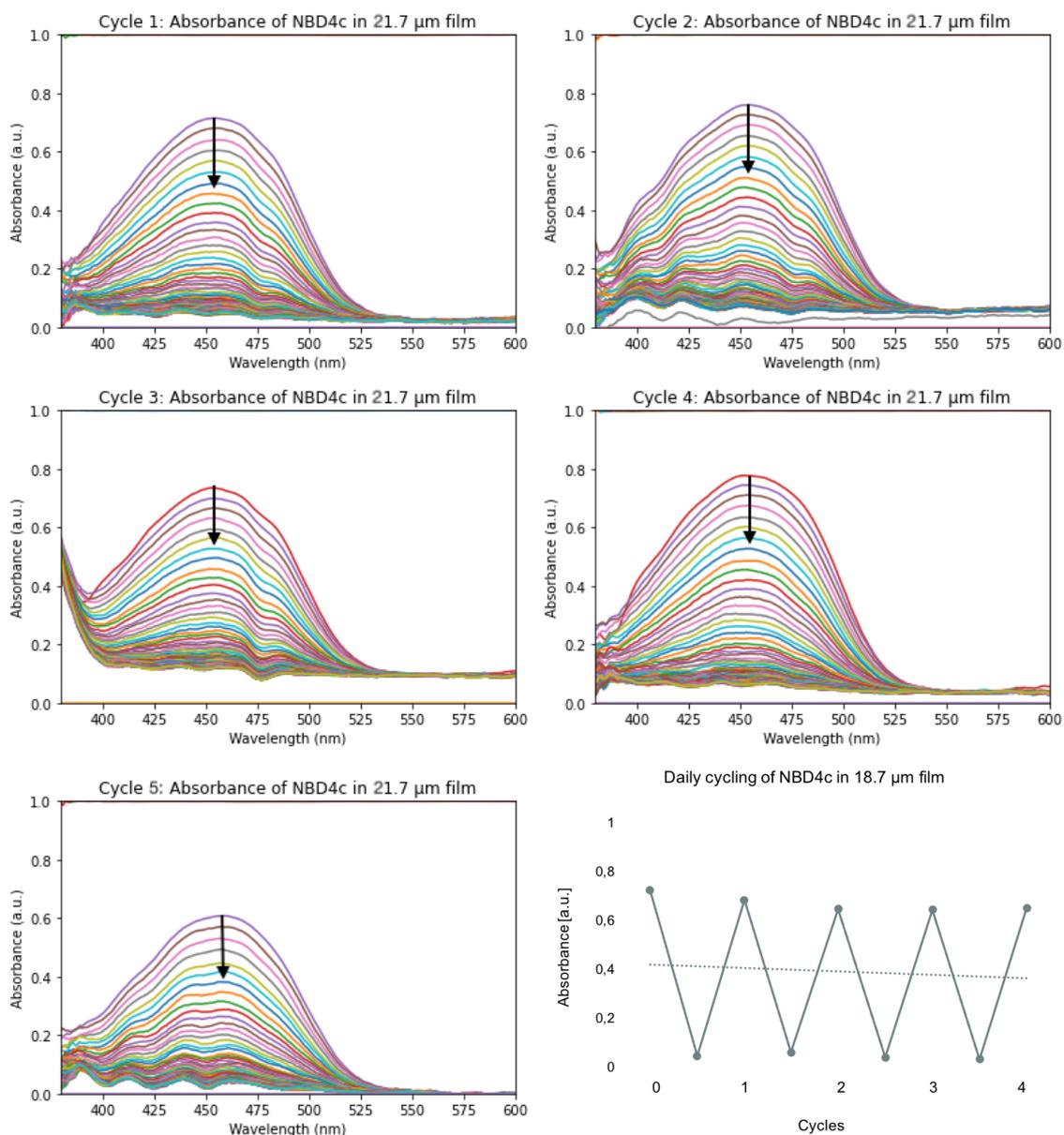


Figure A.1: UV/Vis spectra and cycling analysis of hourly cycles of photoswitch NBD4c in a 21.7 μm film.

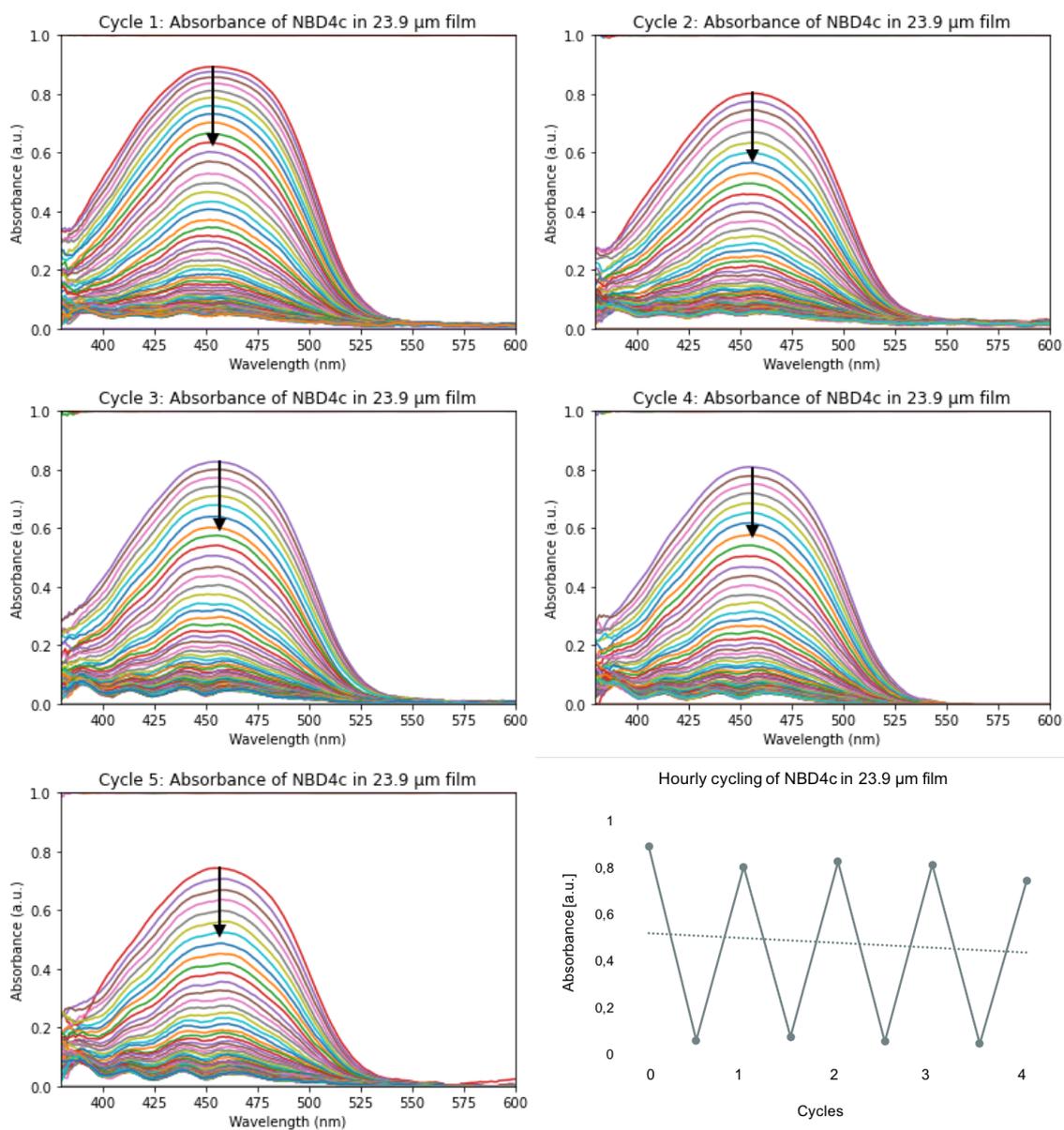


Figure A.2: UV/Vis spectra and cycling analysis of hourly cycles of photoswitch NBD4c in a 23.9 μm film.

A. Appendix 1

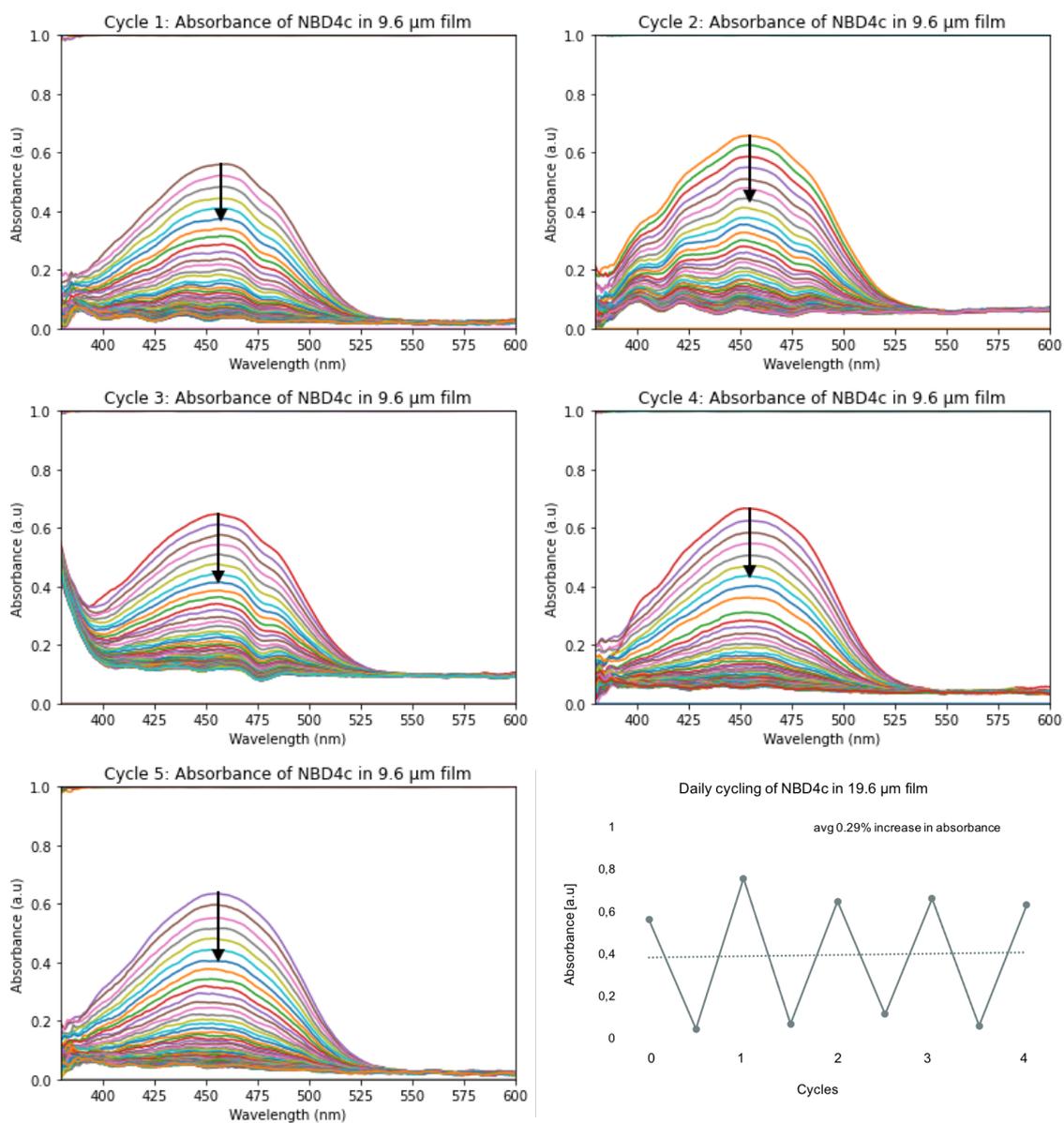


Figure A.3: UV/Vis spectra and cycling analysis of daily cycles of photoswitch NBD4c in a 9.6 μm film.

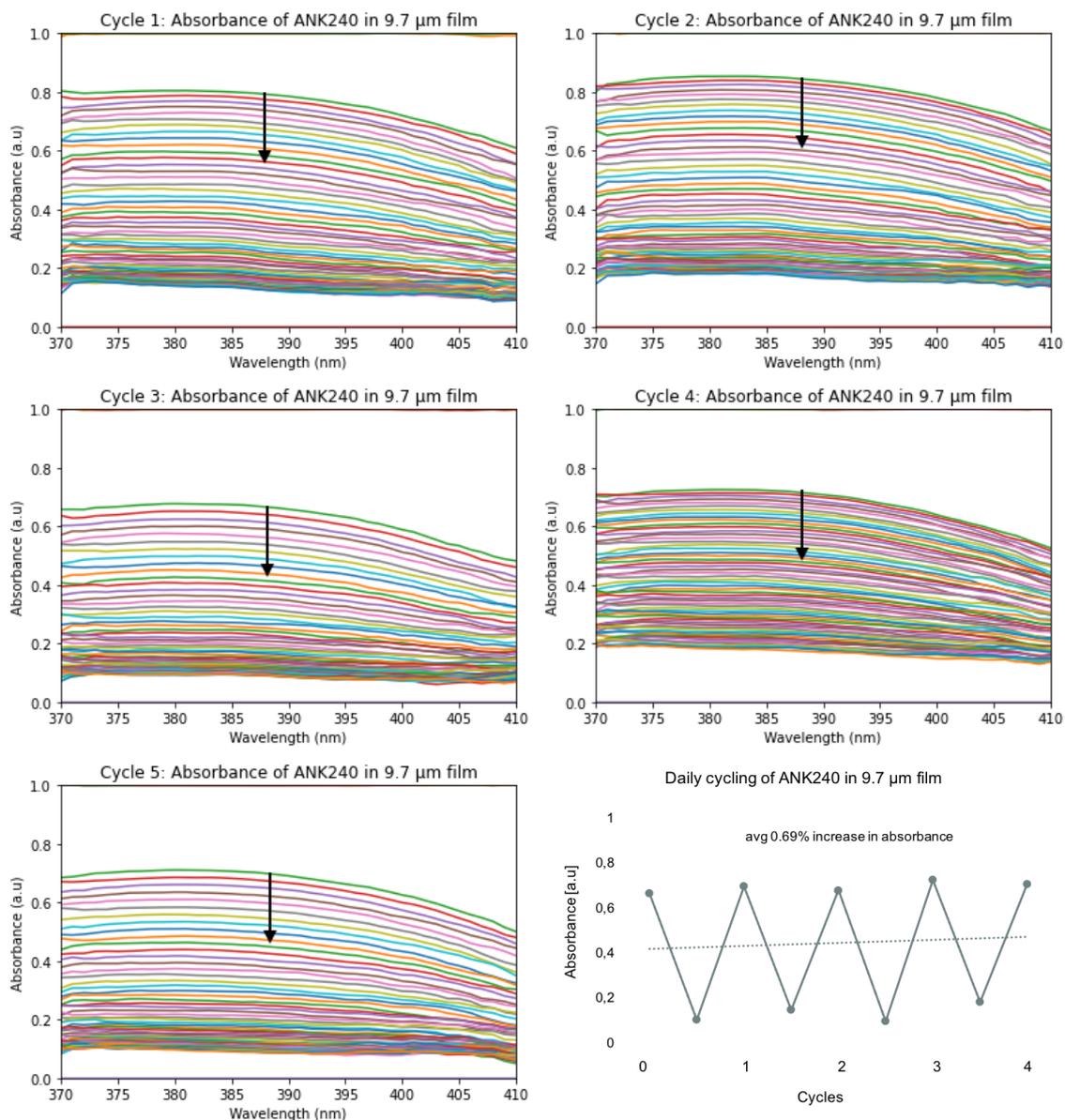


Figure A.4: UV/Vis spectra and cycling analysis of daily cycles of photoswitch ANK240 in a 9.7 μm film.

A.2 UV/Vis Spectra of ANK241

Table A.1: Blade coating parameters and coating results for photoswitch ANK241.

| Sample # | ANK conc. [g cm^{-3}] | Speed [mm s^{-1}] | Film thickness [μm] |
|----------|-------------------------------------|---------------------------------|-------------------------------------|
| 5 | 7.17×10^{-6} | 2 | 15.0 |
| 6 | 7.17×10^{-6} | 5 | 16.4 |

A. Appendix 1

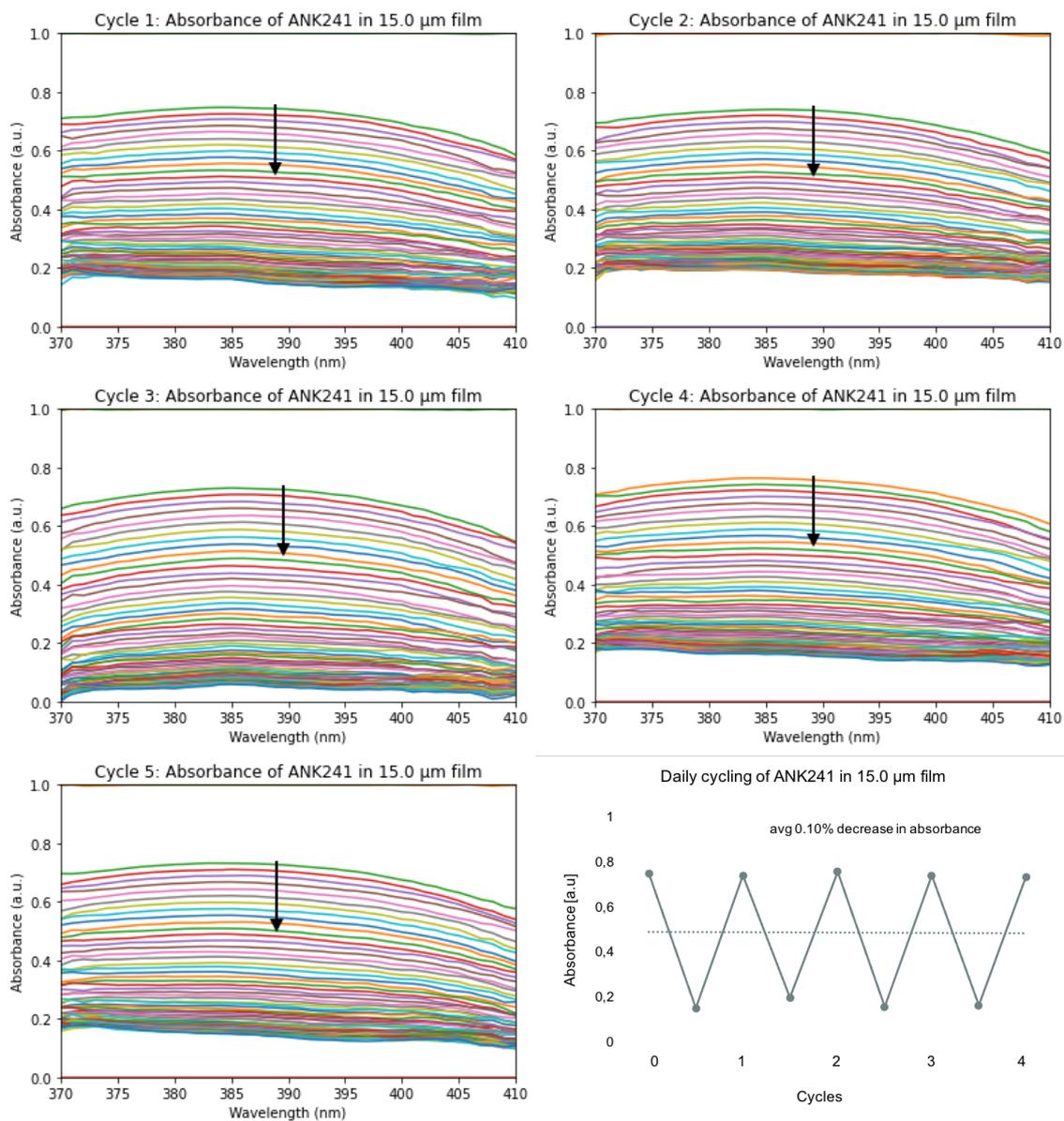
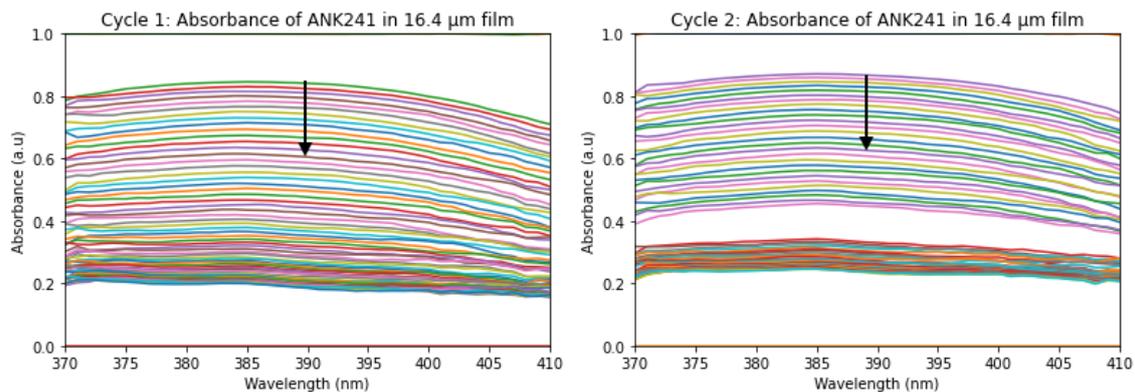


Figure A.5: UV/Vis spectra and cycling analysis of daily cycles of photoswitch ANK241 in a 15.0 μm film.



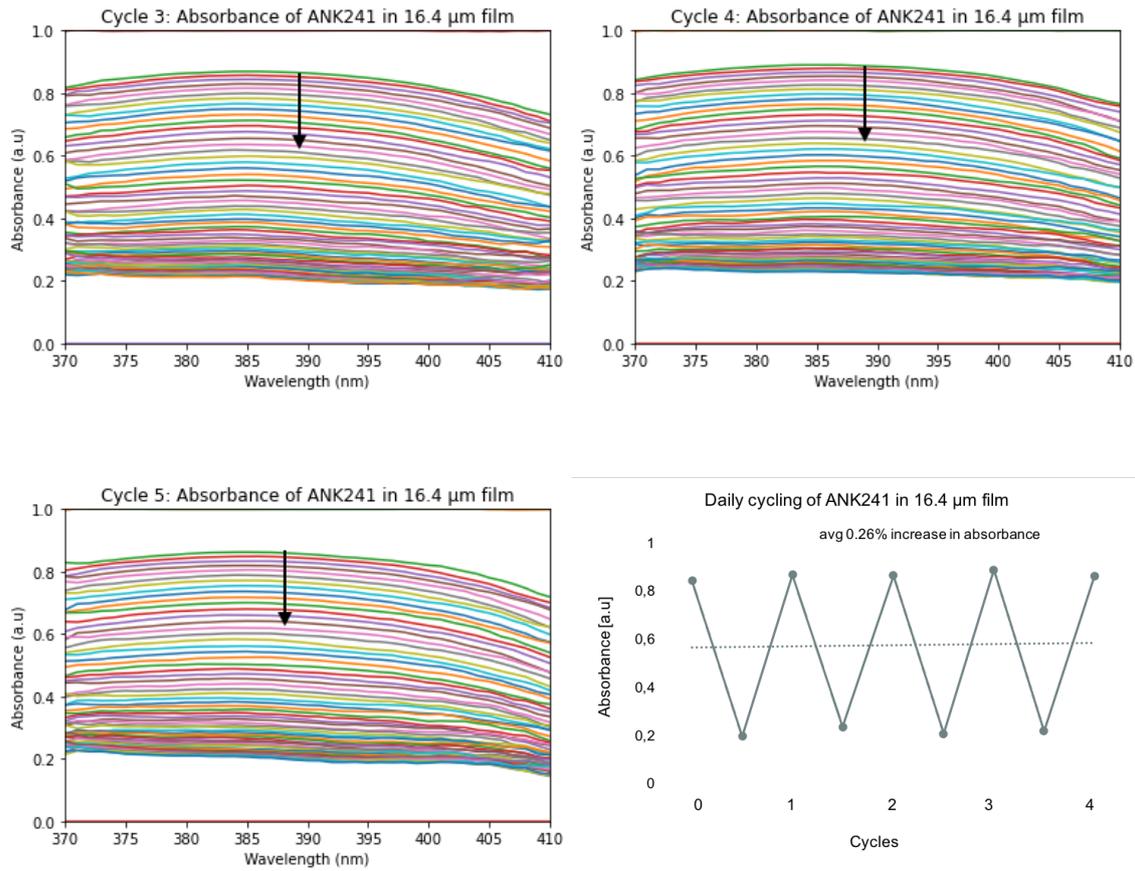


Figure A.8: UV/Vis spectra and cycling analysis of daily cycles of photoswitch ANK241 in a 16.4 μm film.

Table A.2: Properties of ANK241 films and average absorbance differences after cycling measurements without sun exposure.

| Sample # | Film thickness [μm] | NBD conc. [mol cm^{-3}] | Abs diff % |
|----------|-------------------------------------|---------------------------------------|---------------|
| 0 | 15.0 | 5.73×10^{-6} | - 0.10 |
| 2 | 16.4 | 5.73×10^{-6} | + 0.26 |

A.3 UV/Vis Spectra of ANK242

Table A.3: Blade coating parameters and coating results for photoswitch ANK242.

| Sample # | ANK conc. [g cm^{-3}] | Speed [mm s^{-1}] | Film thickness [μm] |
|----------|-------------------------------------|---------------------------------|-------------------------------------|
| 3 | 5.57×10^{-6} | 2 | 9.1 |
| 4 | 5.57×10^{-6} | 5 | 15.8 |

A. Appendix 1

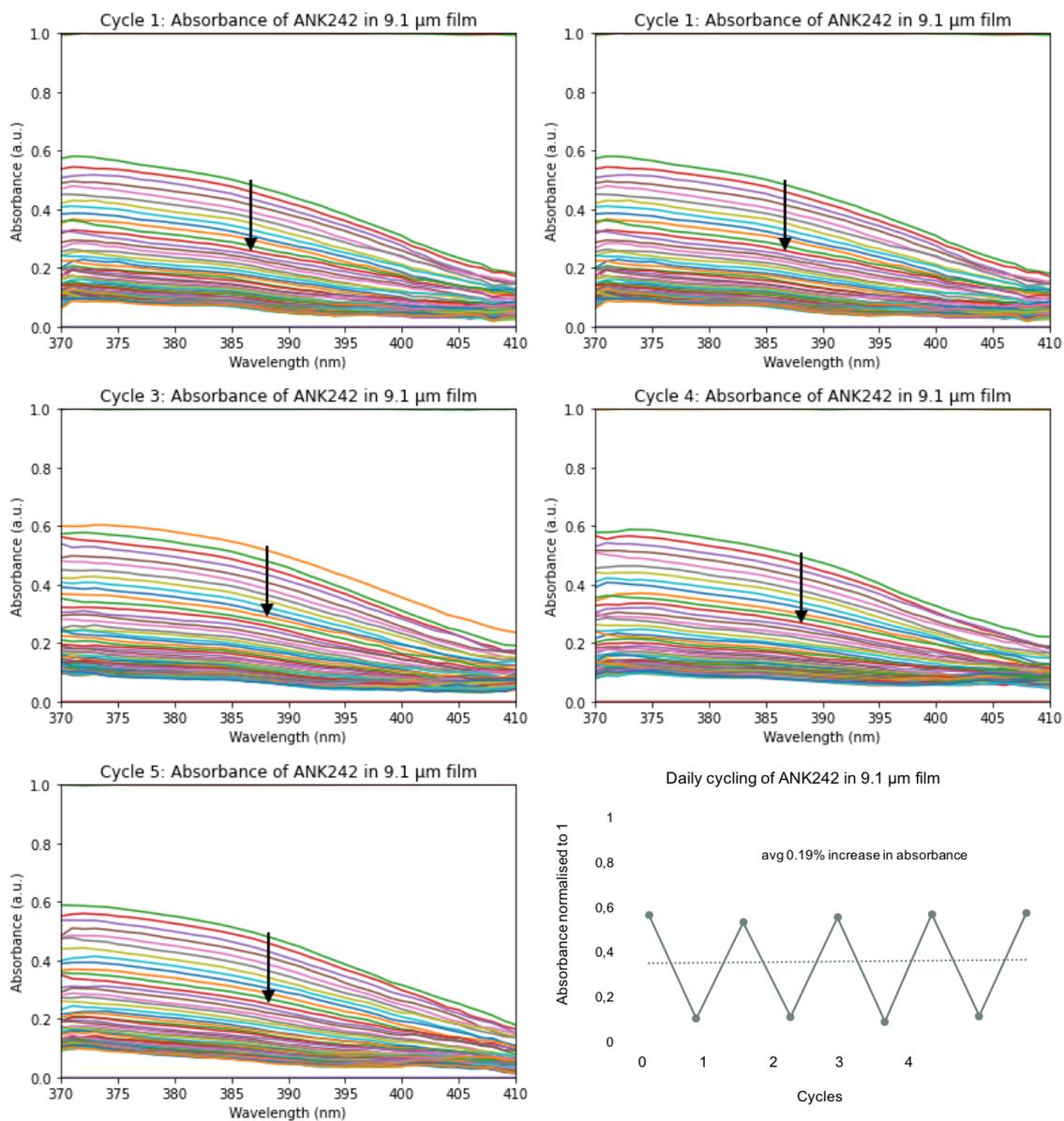
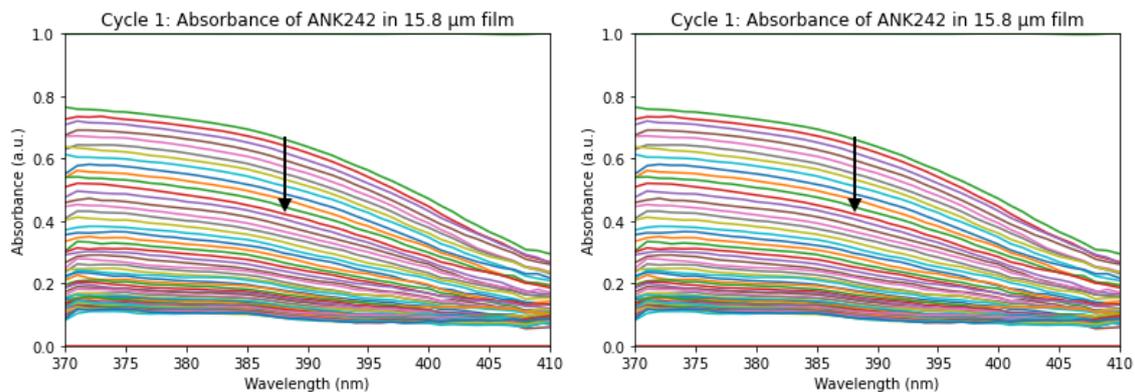


Figure A.9: UV/Vis spectra and cycling analysis of daily cycles of photoswitch ANK242 in a 9.1 μm film.



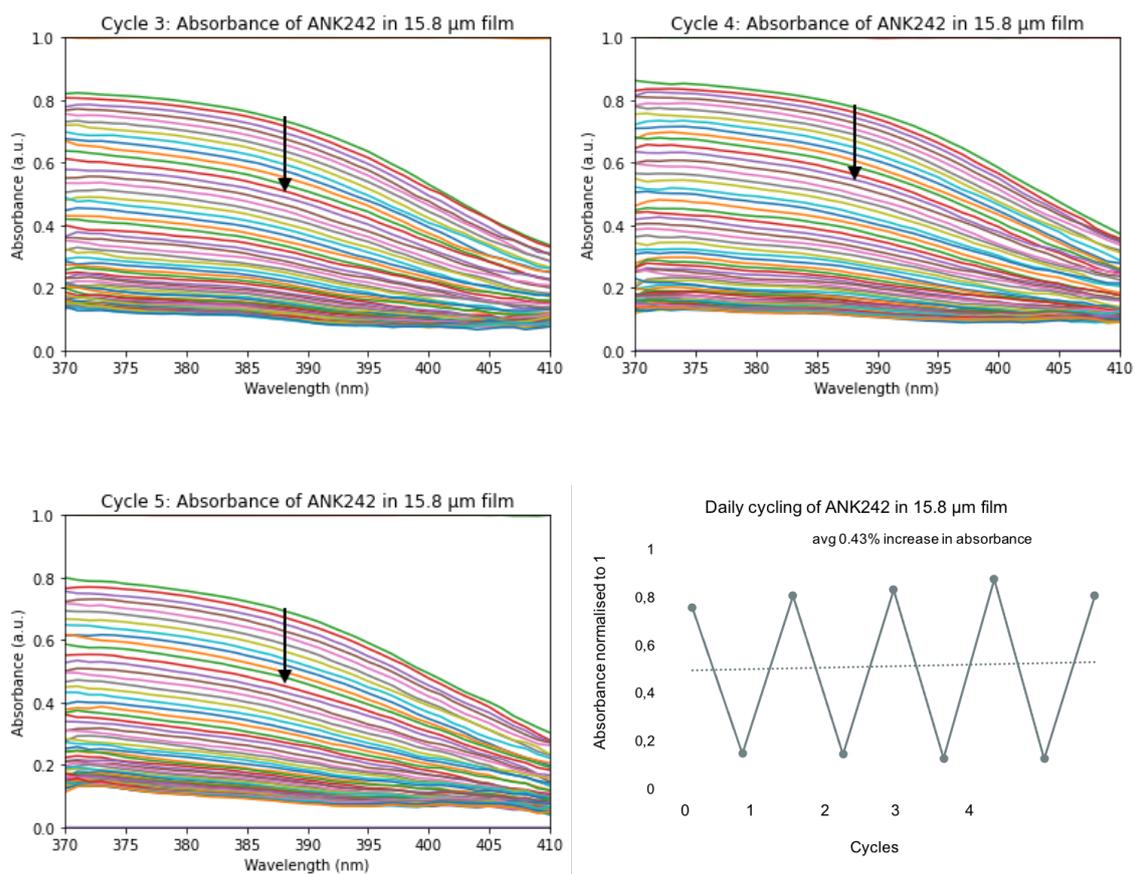


Figure A.12: UV/Vis spectra and cycling analysis of daily cycles of photoswitch ANK242 in a 15.8 μm film.

Table A.4: Properties of ANK242 films and average absorbance differences after daily cycling measurements without sun exposure.

| Sample # | Film thickness [μm] | NBD conc. [mol cm^{-3}] | Abs diff % |
|----------|-------------------------------------|---------------------------------------|---------------|
| 3 | 9.1 | 5.57×10^{-6} | + 0.19 |
| 4 | 15.8 | 5.57×10^{-6} | + 0.43 |

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